PHOSPHORUS IMMOBILIZATION BY CHEMICAL AMENDMENTS IN A CONSTRUCTED WETLAND

By

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To my wife, Angela, and daughters, Elisha Eumi and Katherine Bomi

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Abstract of Dissertation Presented to the Graduate School
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Agricultural lands adjacent to Lake Apopka, Florida, have been converted to a wetland with a goal of treating eutrophic lake water. Flooding of the wetland soil has resulted in a substantial increase in soluble P flux from soil to the overlying water column. A series of laboratory studies were conducted to determine (i) the effectiveness of different chemicals in immobilizing soluble P in recently flooded organic soil, (ii) the effect of chemical amendment application methods on soluble P release to water column, (iii) inorganic P sorption capacity of chemically amended soils and (iv) the P solubility change of chemically amended soils as influenced by soil redox potential.

All amendments ($CaCO_3$, $Ca(OH)_2$, $CaMg(CO_3)_2$, $Al_2(SO_4)_3nH_2O$, $FeCl_3$, and mixtures of $CaCO_3$ with $Al_2(SO_4)_3nH_2O$ and $FeCl_3$) enhanced retention of soluble P, and reduction of the P flux to the overlying water column was dependent on the amount of chemical added. Applications of $CaCO_3$ and $Ca(OH)_2$ at rates of 7 to 15 g kg^{-1} were effective in immobilizing up to 62 and 79 % of dissolved reactive P (DRP), respectively. Higher $CaCO_3$ treatments (> 15 g kg^{-1}) did not immobilize P any greater than 69%, while $Ca(OH)_2$ treatment at 75 g kg^{-1} decreased up to 100% of DRP. Reduction of DRP was proportional to the amount of alum and $FeCl_3$, with up to 80%

of DRP immobilized at rates of 2 and 12 g kg^{-1} of $FeCl_3$ and alum, respectively. Relatively higher amounts of alum were required to minimize DRP concentration in the floodwater as compared with $FeCl_3$ treatments.

In a comparison of chemical application methods, the results obtained from Column study 1 (chemicals were incorporated with whole column soil) and Column study 2 (chemical amendments were applied to the top 3cm of the soil column) were similar. Phosphorus flux from soil to the overlying water column decreased with the application of amendments as follows; $FeCl_3$ (1-2 g kg^{-1}) > alum (14.5 g kg^{-1})> $Ca(OH)_2$ (11.3 g kg^{-1}) >$CaCO_3$ (15.3 g kg^{-1}) > Dolomite (126 g kg^{-1}).

Lake Apopka marsh soil had a high equilibrium phosphorus concentration (EPC_o = 766 μM P), indicating very high water soluble P. The EPC_o is defined as the P concentration at which the rates of adsorption and desorption are equal. Phosphorus sorption capacities (S_{max}) of chemically amended soils obtained from an incubation study ranged from 13 to 44 mmol P kg^{-1} and decreased in the order: alum > $Ca(OH)_2$ > $CaCO_3$ > Dolomite > $FeCl_3$ > controls, while the capacities of retaining adsorbed P decreased in the order: $Ca(OH)_2$ > $CaCO_3$ > alum > dolomite > $FeCl_3$ > controls. The S_{max} of the alum/$FeCl_3$ amended soils was highly correlated with CDB-Al/Fe ($p < 0.01$), Oxalate-Al/Fe ($p<0.05$), and HCl-Al/Fe ($p<0.005$). The S_{max} of the soils amended with Ca-based materials was also highly correlated with water soluble Ca and 1 M HCl-Ca/Mg ($p<0.005$).

Redox potential (Eh) had significant influence on DRP and water soluble Fe of unamended and $FeCl_3$ amended Lake Apopka marsh soils. Concentrations of the DRP and dissolved Fe at -100 mV in porewater were 8 and 10 times higher than those at 350 mV, respectively. The concentrations began to change significantly at Eh of about 200 mV, indicating that Fe oxidation-reduction processes were occurring. The soils treated with alum and $CaCO_3$ were shown to be less sensitive to redox potential changes than control and $FeCl_3$ amended soils.

CHAPTER 1
INTRODUCTION

One of the most important functions of created wetlands is their ability to purify the nutrient (nitrogen [N] and phosphorus [P]) laden water from municipal, industrial, and agricultural activities. Large-scale constructed wetlands are based on surface flow. There is growing interest in converting current agricultural lands (converted from former wetlands) that are adjacent to sensitive aquatic systems back into wetlands to restore their water quality improvement functions. Some examples of such systems in Florida are 1) storm water treatment areas of the Everglades, 2) wetlands created on formerly agricultural lands in the Oklawaha River Basin, and 3) constructed wetlands in agricultural watersheds. Wetland soils that are transformed from agricultural lands contain residual fertilizer-derived nutrients, especially P. Flooding causes solubilization of soil P, resulting in rapid release to the overlying water column. In the start-up phase, many of these wetlands function as a source of P to the water column until the plant and other biotic communities are established and soluble P reaches equilibrium with the solid phase. At present there is growing interest in stabilizing the labile P in these soils by adding chemical amendments.

Nitrogen entering wetlands can be transformed into gaseous forms, and a significant portion can be lost from the system. In contrast, P entering wetlands is stored in aquatic vegetation and microbial biomass, through sorption onto clay and oxyhydroxide surface, and by precipitation with cations such as Ca, Mg, Fe, and Al. In many wetlands, most of the P is stored in an organic pool because of low mineral matter and high organic matter, and the stored organic P is converted to bioavailable P through a relatively slow rate of decomposition under anaerobic conditions (Fig. 1.1). The phosphate ions released through the decomposition of organic matter may be resorbed by clay and hydrous oxides of Al in the anaerobic zone (Gasser and Bloomfield, 1955) or may diffuse to the oxidized zone and precipitated with Fe oxides or Ca compounds (Reddy and D'Angelo, 1994). Inorganic P in wetland soils associated with Ca, Al, Fe, and Mn accounts for <25% of the total P, but most of the studies of P dynamics have focused on inorganic P forms because of their high reactivity and solubility in the soil and water column. Iron (III) and aluminum phosphates release phosphate as pH increases, while calcium phosphates liberate phosphate as pH decreases (Stumm and Morgan, 1981).

In wetland soils, the oxygen supply is limited, which results in the reduction of several other electron acceptors such as nitrate, Fe^{3+}, Mn^{4+}, and SO_4^{2-} . A consequence of reduction is an increase in the concentration of water-soluble and available P. The increase in solubility of P is associated with a decrease of Eh and/or increase of Fe^{2+}, suggesting a role of Fe^{3+}-bound P (Ponnamperuma, 1972). In alkaline soils, the increase in solubility of P is a consequence of the decrease in pH, resulting in solubilization of Ca-bound phosphates as pH decreases (Ferguson, 1977).

Statement of the Problem

Lake Apopka, the fourth-largest lake in Florida and the largest lake in the Oklawaha river basin, is severely degraded. Historically, Lake Apopka was known for bass fishing.

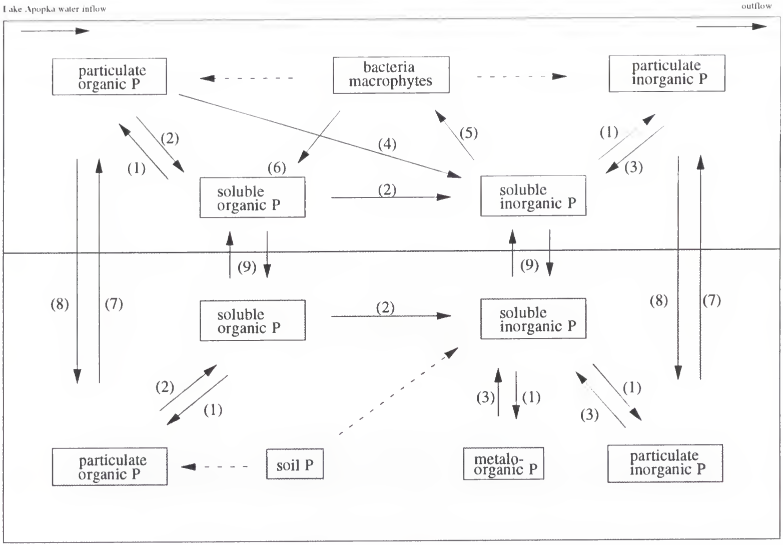

Fig. 1.1. Phosphorus cycle in the created Lake Apopka marsh. (1) adsorption, (2) hydrolysis, (3) desorption, (4) mineralization, (5) assimilation, (6) decomposition, (7) resuspension, (8) sedimentation, and (9) diffusion/mass flow.

In recent years, the bass have been replaced with rough fish such as shad, gar, and catfish (Shannon and Brezonik, 1972). The trophic state index value of Lake Apopka is 86 (Lowe et al., 1988), indicating a hyper-eutrophic status. This index value is the highest among Florida lakes (Huber et al., 1982). Nitrogen- and P-laden agricultural drainage water (76 billion L/yr) was the major external nutrient source to Lake Apopka, representing about 30% of the total N and 58% of the total P inputs (Lowe et al., 1988). Total external P loading to Lake Apopka has been reported to be approximately 68 t P yr^{-1} (Olila, 1992).

During the past few decades, several studies have reported on the use of freshwater wetlands to reduce N and P levels in wastewaters and surface waters (Reddy et al., 1982; Smith, 1989; Turner et al., 1976). Currently this concept is being evaluated as a mechanism to improve the water quality in Lake Apopka, near Orlando, Florida. Agricultural lands adjacent to sensitive aquatic systems are now being acquired by the State of Florida and federal agencies, and, in many cases, these areas are converted back to their natural condition. Eutrophic Lake Apopka water is allowed to flow by gravity through a constructed marsh, and the suspended algal biomass and other detrital materials are allowed to settle on the soil surface (Lowe et al., 1988). However, flooding previously fertilized agricultural land results in solubilization of inorganic P and releases it into the overlying water column. Internal P loading from lake sediments to overlying water is well recognized as the second important factor regulating lake water quality (Reddy, 1990). Similarly, dissolved reactive P (DRP) release from Lake Apopka marsh soil is large enough to cause high P concentrations in the floodwater. Porewater DRP concentrations in the soil (0-20 cm depth) collected from 50 meters (site 2) to 3000 meters (site 5) of the inflow of the Lake Apopka marsh project (Fig. 1.2) ranged from 1 to 31 mg L^{-1} (D'Angelo and Reddy, 1994). The northern area of the marsh (site 5) was of major concern because of its high potential for release of P.

The capacity of wetland soil to maximize nutrient removal depends on the kinetics of biogeochemical processes, which are the interactions between organic and inorganic compounds (Small, 1978; Richardson and Davis, 1987). The factors that regulate water quality of wetlands are 1) soil factors (such as soil physico-chemical properties and associated biogeochemical processes), 2) hydrologic factors (water table fluctuations and hydraulic loading rate) and 3) vegetation factors (such as uptake and decay).

Wetlands themselves may not always provide for a sufficient reduction in the inflow P concentration because of the recycling of nutrient-rich soils or sediments (Cooke et al., 1977) and the limited capacity of soils to retain P (Small and Werm, 1977). Several studies by Kadlec and Tilton (1978), Boyt et al. (1977), and Small (1978) showed high P reduction (>95%), while Fetter et al. (1978) reported a low reduction in total P (13%).

Need for Research

Reduction of P levels through inactivation/precipitation is one of the techniques being evaluated for restoration of excessively eutrophic lakes (Cooke, 1978). Application of chemicals directly to sediments can potentially bind P into insoluble forms, thus decreasing release of P into the water column.

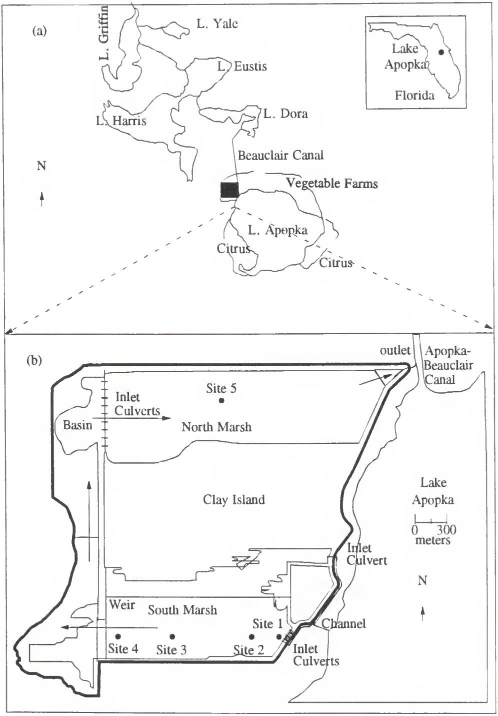

Fig. 1.2. (a) Oklawaha river basin. (b) Flow-way of the created wetland adjacent to Lake Apopka

This concept also can be used in created wetlands containing excessive levels of bioavailable soil P. The soils of the created marsh adjacent to Lake Apopka were used for vegetable production for more than 40 years. The soils have accumulated high P concentrations as a result of many years of fertilizer application. Under flooded conditions, these soils have the potential to release P into the water column. Thus, the soil labile P needs to be decreased to reduce this initial P flux. Natural processes such as uptake by microbes and plants may take several years before this labile P is depleted from the soil. Therefore, it is necessary to create soil conditions to immobilize this P by using techniques such as chemical amendments to supplement the natural functioning of the marsh.

Aluminum (Al) has been used most often in P inactivation/precipitation projects because Al complexes and polymers are inert to redox changes and are effective in entrapment and removal of inorganic and particulate P in the water column (Cooke et al., 1977). Low solubility of Al salts at the pH of natural systems may result in minimal toxicity of Al to aquatic biota. However, the effect of Al on P solubility in marshes is poorly defined, especially in wetland soils having high Ca and Mg concentrations. Calcium additions are known for their effectiveness for P removal in sewage treatment systems. At a high pH (>9), Ca forms amorphous or crystalline P compounds such as dicalcium phosphate, beta tricalcium phosphate, and calcium hydrogen phosphate, followed by crystalline forms of apatite, which is thermodynamically the most stable form in nature (Ferguson et al., 1970). However, such a high pH value in natural waters can result in harmful effects to biological systems. Thus, the selection of proper chemicals depends on the conditions of the wetland systems because each chemical has different effects and associated costs. Optional cost-effective rates of application and long-term stability of these chemicals in binding P needs to be evaluated.

As a first step, the soils in the marsh should be characterized for labile and nonlabile forms. It is necessary to elucidate the role of physico-chemical factors such as redox potential, pH, temperature, and organic matter in immobilizing inorganic P in the soil. Most of the research on P inactivation by chemicals has focused on P removal in the water column rather than P control in the soil/sediment. The effects of applying various chemicals into the soil compartment to immobilize P and the associated biogeochemical processes such as precipitation and adsorption-desorption have not been adequately elucidated. A better understanding of the role of these soil amendments in P inactivation may be achieved by evaluating the biogeochemical processes in the soils that will receive different types of chemicals. Geochemical and mineralogical analysis of the amended soils will provide useful information on the long-term stability of these compounds.

Objectives

Increased P release from flooded organic soils is due to the solubilization of amorphous Fe, Al, and Ca-P compounds and the mineralization of organic P. The soils in the constructed marsh adjacent to Lake Apopka contain high concentrations of Ca and Mg as compared to Fe and Al (Reddy, 1994). However, the concentrations of Fe and Al are believed to be high enough to cause a significant effect on P solubility even though concentrations of water soluble Fe and Al in the water column of the marsh have been shown to be below the detection limit.

Thus, the inorganic P retention capacity of the soils in the created Apopka marsh seemed to be controlled by high Ca and relatively high Al and Fe concentrations in the soils (Reddy, 1994). These soils also contain a large amount of organic matter, a low molar ratio of Ca to Mg, and probably a high partial pressure of carbon dioxide and the presence of organic acids. All of these factors may influence P solubility and result in an increase of bioavailable P.

It also was hypothesized for this study that the application of P-binding chemicals will increase reactive surfaces for P retention. If this hypothesis is true, an adsorption mechanism involving the solid phase, precipitation by metals (Ca, Fe, and Al), and coprecipitation of P with calcite will play major roles in regulating the concentration of the labile pool of P in this organic soil. The formation of amorphous compounds (Ca-phosphates or Fe/Al-phosphates) is expected to occur in the soil and water column. However, the formation of hydroxyapatite may be inhibited in these soils due to a high Mg concentration and the presence of organic acids.

The overall objective of this research was to evaluate ways to immobilize soluble P into nonavailable forms by applying chemical amendments to the soil-water column of a constructed marsh. The specific objectives were to 1) determine the effects of selected inorganic chemical amendments and their effective rates on P solubility, and evaluate methods for applying chemical amendments to the wetland; 2) evaluate the influence of pH and redox potential (Eh) on P solubility in chemically amended soils;

3) determine P fluxes between the overlying water and the soil column and evaluate the stability of phosphate compounds formed in soils amended with P-binding chemicals; and 4) determine the effectiveness of soil amendments in P sorption relating to overlying water quality.

Site Description

Lake Apopka (12,500 ha) is a shallow (mean depth = 1.7 m) lake located in central Florida, approximately 25 km northwest of Orlando (Fig.1.2). Until the 1950s, Lake Apopka attracted national attention as a bass fishing lake. Lake Apopka now attracts statewide attention as an example of the worst effects of cultural eutrophication. About 90% of the lake bottom is covered with organic deposits. Some areas have muck to a depth of 15 m. The surface sediments are unconsolidated and easily suspended into the water column. Half a century ago, the marshes on the north shore of Lake Apopka were converted to farmlands for vegetable production. Lake Apopka water was used for irrigation of the farmland. Thus, pesticides, fertilizers, and soil nutrients entered the lake as the water was pumped off the fields and back into the lake. Because of the size of Lake Apopka and its position as the first lake in the Oklawaha chain of lakes, its restoration is a necessary first step to protect the quality of water in downstream lakes.

The St. Johns River Water Management District has the authority to evaluate the results of restoring a portion of the floodplain marsh under Section 5 of Chapter 85-148, Laws of Florida, 1985. It has proposed state acquisition of up to 32 km^2 (3198 ha) of muck farmland adjacent to Lake Apopka and the creation of a wetland on the acquired land (Fig. 1.2). A demonstration project was established on 749 ha of which about 385 ha was converted into marsh in December 1990. The flow-way will be expanded to 2,024 ha. The water depth in the wetland is 75 cm and flow rate is 14.4 m^3 s^{-1}, and upon full-scale operation this flow rate will allow the entire volume of the lake water to pass through the wetland twice a year. It is estimated that the full marsh project will extract 30 metric tons of P from the lake water annually (Lowe, 1988).

Dissertation format

The dissertation includes six chapters. Chapter 1 has presented a brief introduction including the statement of the problem, need for research, and objectives. The experiments described in Chapter 2 included data collection to determine the effectiveness of various amendments added to soil at different rates. Results of this study formed a basis to develop subsequent experiments. Studies to determine P exchange between the soil and water column as influenced by soil amendments are described in Chapter 3. Chapter 4 provides information about P sorption characteristics of amended soils. Studies described in Chapter 5 were focused on the effects of Eh and pH of chemically amended soils on P solubility. The overall conclusions and significance of results are summarized in Chapter 6.

CHAPTER 2
PHOSPHORUS SOLUBILITY IN CHEMICALLY AMENDED SOILS

Introduction

Phosphorus is present in organic and inorganic forms in wetlands. Both organic and inorganic forms of P are involved in biotic and abiotic transformations in the soil and water column. Organic P comprises a major fraction of the total P in many lakes, rivers, and wetlands. The deposition of dead algal cells or dead plant and animal remains, and partially derived from microbial assimilation of inorganic P during cell synthesis is probably the major source of organic P (Syers et al., 1973). Soil organic P is present in both dissolved and particulate forms (Van Eck, 1982).

The inability of conventional physical-biological wastewater treatment systems to produce low effluent P has resulted in the investigation of P removal by chemical application (Minton et al., 1972). The metal ions present in the water or added to the water system as coagulants are hydrolyzed, forming polynuclear complexes. In particular, polyvalent metal ions are known to form complexes with ionizable functional groups such as hydroxyl, carboxylic, phosphate, and sulfate (Stumm and Mogan, 1962). These results suggest the possibility of using chemical salts to coagulate the impurities in the water treatment systems. The application of metal salts to remove P from the water column was originated from technology that used alum for P removal in advanced wastewater treatment (Kennedy et. al., 1981). Iron (Fe [III]) was first used at Dorrdrecht Reservoir in the Netherlands in 1962, and alum treatment was first attempted in 1968 in Sweden (Sanville et al. 1976). The following coagulants have been tested for P removal of wastewater treatment systems: alum (Cooke et al., 1981), sodium aluminate (Sanville et al., 1976), activated alumina (Convery, 1968), ferric chloride (Dunst, 1974), ferric aluminum sulfate (Foy, 1985), ferrous perchlorate (Singer, 1972), calcium carbonate (Yuan and Lucas, 1989), calcium chloride (Ferguson, 1973), calcium hydroxide (Babin et al., 1989), and zirconium tetrachloride (Peterson, 1976).

The reduction of lake P concentrations through inactivation and precipitation by using chemicals also has been evaluated as a technique for the restoration of excessively eutrophic lakes (Cooke and Kennedy, 1978). This method has focused on procedures to remove P from the water column and control its release from sediments. Unlike in wastewater treatment practices, chemical application to lake waters always have been a concern because of possible negative effects on biota. Alteration in pH and excessive metal concentrations may adversely affect aquatic organisms (Cooke and Kennedy, 1978).

By applying chemicals (e.g., $CaCO_3$, $FeCl_3$, and alum) to the soil/sediment, readily available P is expected to be immobilized. It was hypothesized that the metal ions (Al^{+3}, Ca^{+2}, and Fe^{+3}) in the form of free ions or hydroxides would react with soluble P in the soil. The objective of this laboratory study was to determine the influence of different chemical amendments, applied at various loading rates, on water-soluble P and selected physico-chemical properties of wetland soils.

Materials and Methods

Soil Sampling

The bulk of soil samples (surface to 20 cm depth) were obtained at about 300 m from the inflow of the Lake Apopka marsh (Station 2 in Fig. 2.1). Field moist samples were

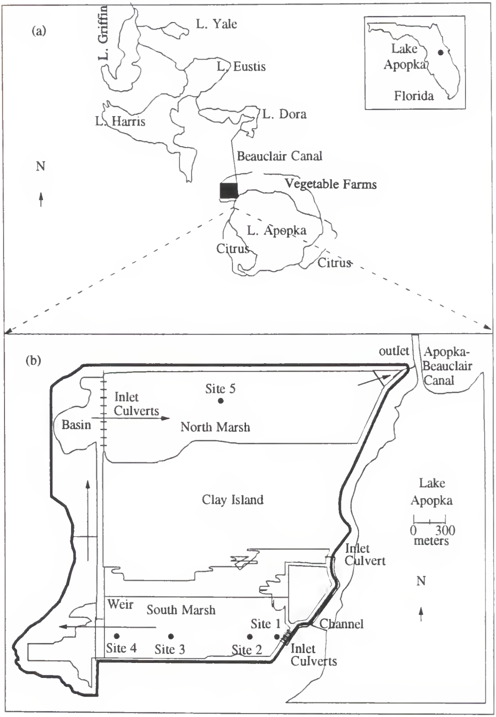

Fig. 2.1. (a) Oklawaha river basin, (b) Flow-way of the created wetland adjacent to Lake Apopka. Soil was obtained from Site 2.

air-dried, pulverized using a mortar and pestle, and then passed through a 20-mesh sieve.

Air-drying was necessary to create preflooding conditions in these soils. The soil was homogenized by mixing thoroughly and then stored in plastic bags at 4^{o}C until used in the batch incubation experiments.

Soil Characteristics

Soil pH, water content, and organic matter content. Soil pH was measured at a 1:1 soil to water ratio using a combination glass electrode and pH meter. Organic matter was determined by combusting known amounts of air-dried samples in a furnace at 550^{o} C for 5 hours (APHA, 1985). The loss in weight after combustion was calculated and expressed as the percentage of volatile solids. The water content of both fresh and air-dried samples was determined by oven-drying at 80^{o}C for 72 hours or until a constant weight was recorded.

Water soluble P and selected cations. A 0.2 g air-dried soil sample plus 20 ml distilled/deionized (DDI) water was placed in 50 ml centrifuge tubes, shaken in end to end shaker for 3 hours, and then centrifuged for 15 min at 6,000 rpm. The supernatant liquid was filtered through a 0.45 μm membrane filter. The extracts were analyzed for dissolved reactive P (DRP) using standard methods (APHA, 1985). The concentrations of Ca, Mg, Al, and Fe in the extracts also were determined using atomic absorption spectroscopy.

HCl-extractable P and selected cations. A 0.2 g air-dried soil sample was treated with 20 ml of 1M HCl and shaken for 3 hours, followed by filtration through a 0.45 μm membrane filter. The extracts were analyzed for DRP and selected cations as described above.

Total P and selected cations. A 0.4 g air-dried soil sample placed in a 50 ml beaker was combusted in the furnace at 550°C for 5 hours. The combusted sample was treated with 20 ml of 6 M HCl solution and dried on a hot plate at a low temperature. After the beaker cooled, 2.25 ml of 6 M HCl solution was transferred into the beaker and heated until just before the boiling point (Anderson, 1976). The sample was then filtered through a Whatman No. 40 filter and diluted to 50 ml with DDI water. The extracts were analyzed for total P using the ascorbic acid method with the autoanalyzer, and for cations by using atomic absorption spectroscopy.

Laboratory Incubation

A known amount (5 g) of air-dried soil was placed into a 50ml centrifuge tube containing precalculated amounts of chemical amendments and treated with 25 ml of DDI water. Pure compounds of calcium carbonate ($CaCO_3$), calcium hydroxide ($Ca(OH)_2$), alum ($Al_2(SO_4)_38H2O$), ferric chloride ($FeCl_3$), and alum/calcium carbonate mixtures were used in the study. Three replications of the following chemical treatments were used. On an areal basis (bulk density of soil = 0.25 g cm^{-3} and 20 cm soil depth), 1g kg^{-1} of amendment is equal to 50 g m^{-2}.

(1) $CaCO_3$: (0, 8.9, 11.5, 15.2, 22.9, 40.3, 57.6, and 101.9 g kg^{-1} of soil)

(2) $Ca(OH)_2$: (0, 6.7, 8.6, 11.3, 17.3, 29.9, 42.7, and 75.7 g kg^{-1} of soil)

(3) Alum: (0, 1.4, 3.6, 7.2, 14.4, and 21.8 g kg^{-1} of soil)

(4) $FeCl_3$: (0, 0.7, 1.8, 3.6, 7.2, and 10.6 g kg^{-1} of soil)

(5) Alum (1.4) + $CaCO_3$ (11.5, 23, 40.3, and 57.5, g kg^{-1} soil)

(6) Alum (23.6) + $CaCO_3$ (1.5, 23, 40.3, and 57.5, g kg^{-1} soil)

(7) Alum (14.5) + $CaCO_3$ (11.5, 23, 40.3, and 57.5, g kg^{-1} soil)

The soil suspensions were incubated on a mechanical shaker at 25°C for a period of 3 days. After the incubatioin period, soil suspensions were centrifuged at 6,000 rpm for 15 minutes and the supernatant liquid was filtered through a 0.45 μm membrane filter. The filtrates were acidified to about pH 2 with one drop of concentrated H_2SO_4 (Baker Ultrapure) and stored at 4°C until analyzed for DRP by using an automated ascorbic acid method.

Mineral Equilibria

The computer program SOILCHEM (Sposito and Coves, 1991) was used to predict the chemical speciation of P in the liquid phase. Input to the program consisted of the measured concentrations of Al, Ca, Fe, K, Na, Mn, Mg, Zn, P, dissolved inorganic C, Cl, and pH. Activity coefficients were calculated using the Davies equation (Stumm and Morgan, 1981), and ionic strength was calculated using SOILCHEM (Sposito and Coves, 1991). When calculating ion activities, precipitation was assumed not to occur.

Results

Physico-chemical Properties of Soils

Selected chemical characteristics of the soil used are shown in Table 2.1. Total inorganic P represented approximately 22% of the total P. About 16% of total P and 73% of total inorganic P were found in the water-extractable fraction. Dissolved reactive phosphorus (DRP) concentration in the water column of Lake Apopka marsh was 0.22

Table 2.1. Some physico-chemical properties of water and soil samples obtained from Site 2 of Lake Apopka Marsh Flow-way Demonstration Project.

Properties		Water Sample	Soil Sample
Bulk density	(g cm^{-3})		0.25
Water content	(g kg^{-1})		830
pH		6.5	5.55
Ec	(mS m^{-1})	28	
Dissolved Reactive	P (mM)	0.007	
Dissolved	Ca	0.77	
	Mg	0.45	
Water Extractable	P (mmol kg^{-1})		1.9
	Ca		12
	Mg		7.2
	Fe		0.02
1 M HCl extractable	P (mmol kg^{-1})		2.6
	Ca		728
	Mg		161
	Fe		21
	Al		28
Total	P (mmol kg^{-1})		12
	Ca		949
	Mg		199
	Fe		35
	Al		98

mg L^{-1}. Surface water pH was 6.5, whereas the soil pH of air-dried soils was in the range of 5.5 to 5.8.

Calcium and Mg were the dominant cations in the water and HCl extracts (Table 2.1). About 1.6% and 4.5% of acid extractable Ca and Mg, respectively, were shown to be water soluble. Aluminum and Fe were below detection limits in water-soluble forms, indicating that the activities of Al (III) and Fe (III) in solution may be limited in slightly acidic to neutral solutions (Hsu, 1964). Minimum solubilities of Al and Fe were reported to be at pH 6 and 5.4, respectively (Snoeyink and Jenkins, 1980). Also, most of the Al and Fe may be filtered through a 0.45 μm membrane filter because of their solid forms, such as Al and Fe hydroxides and oxyhydroxides under aerobic conditions (Nealson and Saffarini, 1994). The fixation of P by Al and Fe probably is dependent on the activities of amorphous Al hydroxides and Fe oxides rather than those of the soluble Al^{3+} and Fe^{3+} (Hsu, 1965).

The calculated molar ratio of total Ca to Mg was found to be 5:1, whereas total Al and Fe were found to be in a 3:1 ratio. In floodwater, the molar ratio of water soluble Ca to Mg was 2:1. Such low ratios in the water column and water extracts may suggest competition between Mg and Ca to combine with P, resulting in P release to the overlying water.

More than 60% of the total Ca, Mg, and Fe in soils was extracted with 1 M HCl, where only 29% of the total Al was extractable, suggesting the relative stability of Al complexes.

Dissolved Ca, Mg, and Inorganic Carbon (DIC) Concentrations in the Soil Solution

The amount of Ca and Mg released from unamended soil was about 10.5 and 4.0 mmol kg^{-1}, respectively (Table 2.2). Generally the solubility of Ca and Mg in the soil solution was increased as chemical amount of $CaCO_3$, $Ca(OH)_2$, $FeCl_3$, and alum increased. Soils amended with alum and $FeCl_3$ had higher solubilities of Ca and Mg than soils receiving Ca-based amendments. In particular, soils amended at rates higher than about 44 mmol kg^{-1} of alum and $FeCl_3$ treatments released more Ca and Mg than soils amended with Ca-based materials (Table 2.2). About 22 to 27 mmol Ca kg^{-1} was released from the soils amended at the highest amount of $CaCO_3$ and $Ca(OH)_2$ (about 1020 mmol Ca kg^{-1}), while 58 and 72 mmol Ca kg^{-1} soil were released from the soils amended with highest amount of alum and $FeCl_3$ (65 mmol Al or Fe kg^{-1}). Maximum solubility of Mg^{2+} in soils amended with $CaCO_3$ was 3.8 mmol kg^{-1}, while the addition of higher than 577 mmol kg^{-1} of $Ca(OH)_2$ decreased Mg solubility to 0.5 mmol kg^{-1}.

Trends similar to water-soluble Ca and Mg were observed in pH in soils amended with Ca-based materials (Fig. 2.2 a, b). In soils amended with alum and $FeCl_3$ a decrease in pH was coupled with a substantial increase of water soluble Ca and Mg (Fig. 2.2 c, d). Calcium carbonate amendment of up to 15.2 g kg^{-1} soil increased water soluble Ca and Mg (Fig. 2.2 a). In soils treated with $Ca(OH)_2$, Ca concentration rapidly increased up to pH 7, followed by a slower rate of increase as the soil pH increased to 9. However, Mg concentration decreased sharply at soil pH higher than 7 (Fig. 2.2 b). Water-soluble Ca and Mg increased with increased rates of alum and $FeCl_3$ application to soil. The increase in Ca and Mg in these soils was inversely related to pH (Fig. 2.2 c,d). Molar ratios of

Table 2.2. Effect of chemical amendments on Ca and Mg solubility in the soil solution.

Treatments	Rate		Metals in soil solution after 3 days of incubation			
			Ca	Mg	pH	[Ca]/[Mg]
	(g kg^{-1})	(mmol kg^{-1})	(mmol kg^{-1})	(mmol kg^{-1})		
$CaCO_3$	0.00	0.00	10.3	4.0	5.50	2.60
	9.00	90.0	15.1	5.2	6.07	2.90
	11.5	115	18.6	6.3	6.14	2.95
	15.2	152	21.9	7.1	6.17	3.00
	23.0	230	22.4	7.2	6.20	3.10
	40.4	404	23.4	7.5	6.30	3.12
	57.6	576	23.8	7.7	6.28	3.10
	102.0	1019	22.6	7.8	6.30	2.90
$Ca(OH)_2$	0.00	0.00	10.3	4.0	5.50	2.60
	6.70	90.0	13.0	4.4	6.12	2.95
	8.60	116	14.0	4.5	6.20	3.11
	11.3	153	16.1	5.1	6.44	3.15
	17.3	233	19.7	5.7	6.95	3.45
	30.0	404	20.6	5.4	7.60	3.83
	42.7	577	22.6	3.4	8.38	6.60
	75.7	1022	26.8	0.5	9.70	53.6
Alum	0.00	0.0	10.5	3.80	5.50	2.76
	1.40	4.0	14.2	5.40	5.49	2.63
	3.60	10	19.4	7.60	5.40	2.55
	7.20	21	29.1	11.2	5.33	2.59
	14.4	43	49.5	18.3	5.14	2.70
	21.8	66	71.8	25.3	4.95	2.84
$FeCl_3$	0.00	0.0	10.5	3.80	5.50	2.76
	0.70	4.0	13.5	5.20	5.43	2.59
	1.80	11	17.1	6.80	5.35	2.51
	3.50	22	27.3	10.9	5.21	2.50
	7.10	44	40.5	15.9	5.02	2.55
	10.5	65	57.9	22.1	4.85	2.62

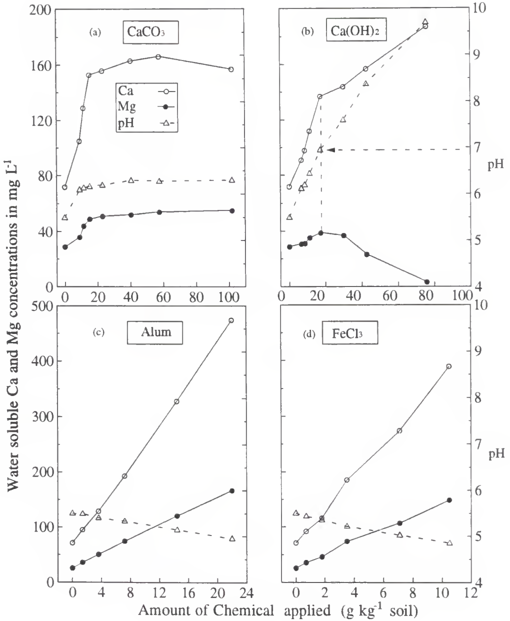

Fig. 2.2. Effects of various chemical treatments on pH and water soluble Ca and Mg in the soil solution.

Ca to Mg in the soil treated with all amendments were in the range of 2.5 to 3.2 in the pH range of 4.9 to 6.4 (Table 2.2).The ratio gradually increased to pH 8.5, followed by a rapid increase in soil treated with $Ca(OH)_2$ (Fig. 2.3 a). This was probably due to a decrease in Mg solubility at high pH. The soil treated with $Ca(OH)_2$ decreased DRP as the ratio of Ca to Mg increased (Fig. 2.3 b).

The concentration of dissolved inorganic carbon (DIC) in soil increased with $CaCO_3$ amendments, whereas the concentration in soil treated with $Ca(OH)_2$ increased only at lower rates where pH was less than 7.6. Higher pH values (8.35) resulting from higher rates of $Ca(OH)_2$ amendment resulted in a decrease in DIC in soil solution (Fig. 2.4 b). This was well balanced with the decreased Ca concentration (Fig. 2.2 b), indicating a formation of crystalline carbon mineral in soil solution amended with $Ca(OH)_2$.

Water soluble P

Addition of chemical amendments generally decreased water soluble P (Tables 2.3 to 2.5). About 60% of the water-soluble P was removed by $CaCO_3$ treatment at 15.2 g kg^{-1}, and subsequent increases in $CaCO_3$ application did not result in an appreciable reduction in water-soluble P (Table 2.3 and Fig. 2.5 a). A linear increase in water-soluble P removal was observed with increased rates of $Ca(OH)_2$ amendment of up to 17.3 g kg^{-1}. Negligible levels of water-soluble P was observed at the highest level of $Ca(OH)_2$ application (75.7 g kg^{-1}) (Table 2.3 and Fig. 2.5 b). The pH of soil solution treated with $CaCO_3$ was buffered at 6.2, while the addition of $Ca(OH)_2$ increased soil pH up to 9.7 (Fig. 2.5 a, b).

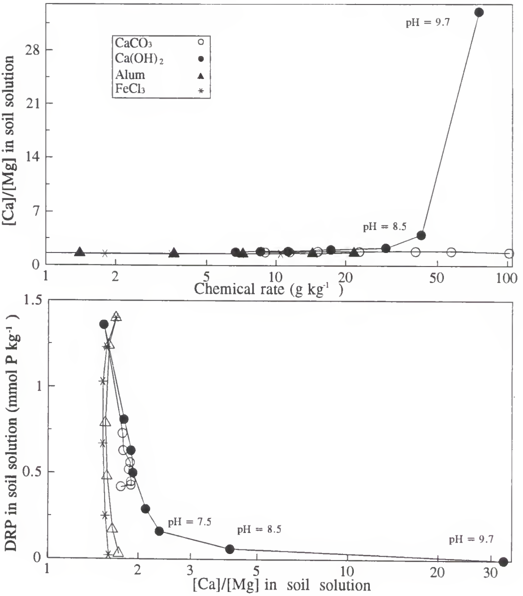

Fig. 2.3. Relationships between DRP and ratio of [Ca] to [Mg] in the soil solution as influenced by using various chemically amended soils.

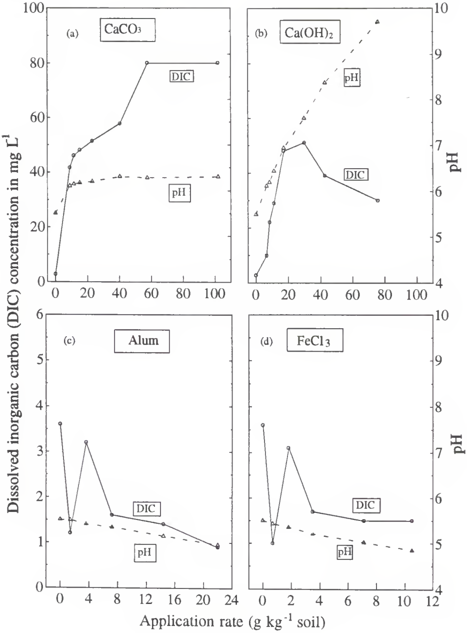

Fig. 2.4. Dissolved inorganic carbonate concentration and pH in soil solution, as influenced by chemically amended soils.

Table 2.3. Effect of calcium based amendments on water soluble P in Lake Apopka marsh soils.

Chemicals Used	Amount of Application		Dissolved reactive P remaining after 3 days			pH
	(g kg^{-1})	Ca^{2+}(mmole kg^{-1})	(mg P kg^{-1} soil)	(mmoles P kg^{-1} soil)	%	
$CaCO_3$	0	0	42.2 ± 3.0	1.36	100	5.50 ± 0.02
	9.0	89	22.5 ± 2.4	0.73	53.5 ± 5.7	6.07 ± 0.00
	11.5	115	19.6 ± 0.03	0.63	46.4 ± 0.8	6.14 ± 0.01
	15.2	152	17.3 ± 0.6	0.56	40.9 ± 1.5	6.17 ± 0.01
	23.0	229	16.1 ± 0.5	0.52	38.1 ± 1.2	6.20 ± 0.00
	40.4	404	13.9 ± 0.2	0.45	33.0 ± 0.6	6.30 ± 0.00
	57.6	576	13.4 ± 0.3	0.43	31.8 ± 0.6	6.28 ± 0.03
	102.0	1019	12.9 ± 1.0	0.42	30.7 ± 2.3	6.30 ± 0.00
$Ca(OH)_2$	0	0	42.2 ± 0.0	1.36	100	5.50 ± 0.02
	6.7	90	25.1 ± 0.1	0.81	59.6 ± 0.1	6.12 ± 0.01
	8.6	116	19.5 ± 1.0	0.63	46.2 ± 2.3	6.20 ± 0.01
	11.3	153	15.5 ± 0.1	0.50	36.6 ± 0.1	6.44 ± 0.01
	17.3	233	9.0 ± 0.5	0.29	21.4 ± 1.1	6.95 ± 0.00
	30.0	404	4.9 ± 0.2	0.16	11.5 ± 0.4	7.60 ± 0.13
	42.7	577	1.7 ± 0.1	0.06	4.2 ± 0.2	8.38 ± 0.08
	75.7	1,022	0.0 ± 0.0	0.00	0.0 ± 0.0	9.77 ± 0.06

Table 2.4. Effect of alum and ferric chloride on dissolved reactive P in Lake Apopka marsh soils.

Chemical Used	Rate of application		Dissolved reactive P remaining after 3 days			pH
	(g kg^{-1})	Al or Fe (mmole kg^{-1})	(mg P kg^{-1} soil)	(mmoles P kg^{-1} soil)	%	
Alum	0	0	43.5 ± 3.0	1.40	100	5.50 ± 0.00
	1.4	4	38.5 ± 1.7	1.24	88.3 ± 4.0	5.49 ± 0.00
	3.6	10	24.5 ± 2.4	0.79	58.4 ± 5.5	5.40 ± 0.00
	7.2	21	15.0 ± 0.1	0.48	34.5 ± 0.3	5.33 ± 0.22
	14.4	43	5.3 ± 0.3	0.17	12.0 ± 0.8	5.14 ± 0.02
	21.8	66	1.0 ± 0.2	0.03	2.0 ± 0.4	4.95 ± 0.00
$FeCl_3$	0	0	43.5 ± 3.0	1.40	100	5.50 ± 0.00
	0.7	4	38.1 ± 1.5	1.23	87.6 ± 3.5	5.43 ± 0.08
	1.8	11	32.0 ± 0.6	1.03	73.6 ± 1.5	5.35 ± 0.00
	3.5	22	20.9 ± 0.7	0.67	48.0 ± 1.5	5.21 ± 0.01
	7.1	44	7.9 ± 0.0	0.25	18.1 ± 0.0	5.02 ± 0.01
	10.5	65	0.71 ± 0.0	0.02	1.6 ± 0.0	4.85 ± 0.00

Table 2.5. Effect of $CaCO_3$ and alum mixtures on dissolved reactive P in Lake Apopka marsh soils.

Chemical Used	Rate of Application				Dissolved reactive P remaining after 3 days			
	$CaCO_3$ (g kg^{-1})	alum (g kg^{-1})	Ca (mmoles kg^{-1})	Al (mmoles kg^{-1})	(mg P kg^{-1})	(mmoles kg^{-1}	(%)	pH
$CaCO_3$ + alum								
	0	0	0	0	50.4 ± 1.5	1.63	100	5.44 ± 0.02
	11.5	1.2	115	4	16.5 ± 2.7	0.53	32.8 ± 3	5.97 ± 0.03
	23.0	1.2	229	4	11.5 ± 2.7	0.37	22.9 ± 5	6.16 ± 0.04
	40.4	1.2	404	4	11.2 ± 1.3	0.36	22.2 ± 5	6.15 ± 0.00
	57.6	1.2	576	4	11.4 ± 0.9	0.37	22.6 ± 7	6.14 ± 0.01
	11.5	3.1	115	10	9.6 ± 2.4	0.31	19.1 ± 4.8	5.63 ± 0.01
	23.0	3.1	229	10	7.7 ± 1.4	0.25	15.1 ± 2.7	5.86 ± 0.04
	40.4	3.1	404	10	8.1 ± 1.0	0.26	15.9 ± 2.1	5.84 ± 0.01
	57.6	3.1	576	10	6.1 ± 0.8	0.20	12.1 ± 1.6	5.88 ± 0.06
	11.5	12.6	115	43	1.19 ± 0.3	0.04	2.4 ± 0.6	5.75 ± 0.00
	23.0	12.6	229	43	0.86 ± 0.4	0.03	1.7 ± 0.7	6.17 ± 0.03
	40.4	12.6	404	43	0.65 ± 0.1	0.02	1.3 ± 0.2	6.14 ± 0.02
	57.6	12.6	576	43	0.74 ± 0.2	0.02	1.5 ± 0.3	6.20 ± 0.01

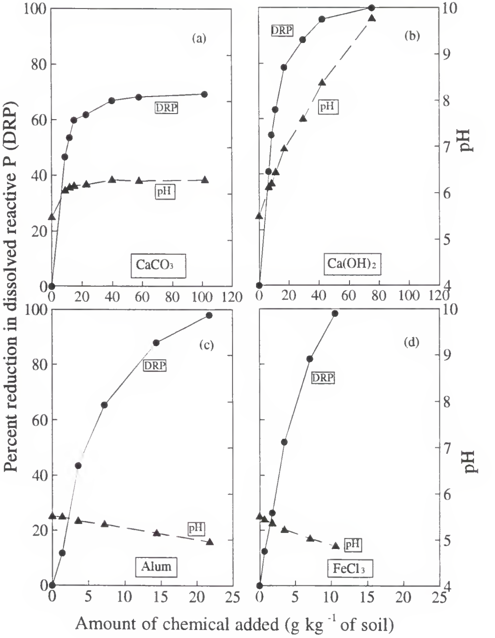

Fig. 2.5. Percent reduction of DRP and pH changes in the soil solution as influenced by using various chemically amended soils. The percent reduction at each treatment was calculated based on the DRP concentration of the control.

Alum and $FeCl_3$ also were effective in reducing DRP concentrations, and the removal of the DRP was directly proportional to the amount of added (Fig. 2.5 c, d). Applications higher than about 12.5 and 7.1 g kg^{-1} of alum and $FeCl_3$ were needed, respectively, to remove about 80% of water soluble P (Fig. 2.5 c, d and Table 2.4). Also, pH reductions in the soil solution were linear with the amount of alum and $FeCl_3$, but the slopes were very low (Fig. 2.5 c, d). The mixtures of alum and $CaCO_3$ (Fig. 2.6 a, b, c) removed more water soluble P than the individual amendment (Fig. 2.5 a, c). For example, the mixtures of 23 g kg^{-1} of $CaCO_3$ and 1.2 g kg^{-1} of alum reduced water soluble P by 77% as compared to individual applications of these chemicals (Table 2.3 to 2.5). However, applications with higher than 11.5 g kg^{-1} of $CaCO_3$ in the mixture ($CaCO_3$/alum) did not significantly increase the removal of water-soluble P (Fig. 2.6 a, b, c). A relatively high amount of alum was needed to remove the water soluble P. The mixtures of two chemicals ($CaCO_3$ and alum) maintained the soil pH around neutral.

Water soluble Ca and Mg were inversely related to the DRP of the soils treated with $CaCO_3$,$Ca(OH)_2$ (Fig. 2.7 a, b), alum, and $FeCl_3$ (Fig. 2.8 a, b).

Solubility of P Compounds

The solubility diagram of Ca, Al, and Fe phosphates calculated based on the equilibrium constants of each compound (Lindsay, 1970) in soils treated with various chemical amendments is presented in Fig. 2.9. In unamended soil, P compounds appeared to be in equilibrium with respect to apatite, but increased amounts of $Ca(OH)_2$ amendments resulted in supersaturation with respect to β-tricalcium phosphate (β-TCP)

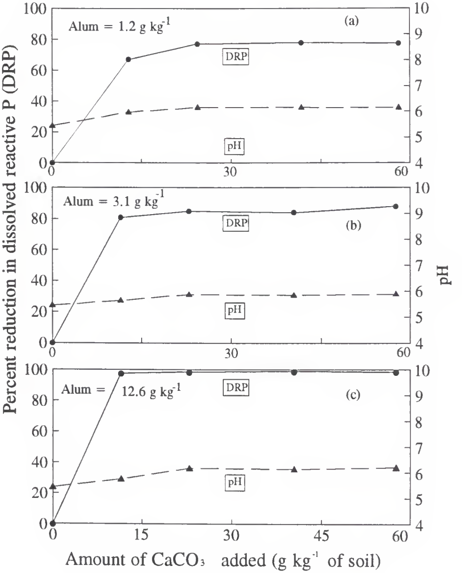

Fig. 2.6. Percent reduction of DRP and pH changes in the soil solution as influenced by using the mixtures of $CaCO_3$ and alum. The percent reduction at each treatment was calculated based on the DRP concentration of the control.

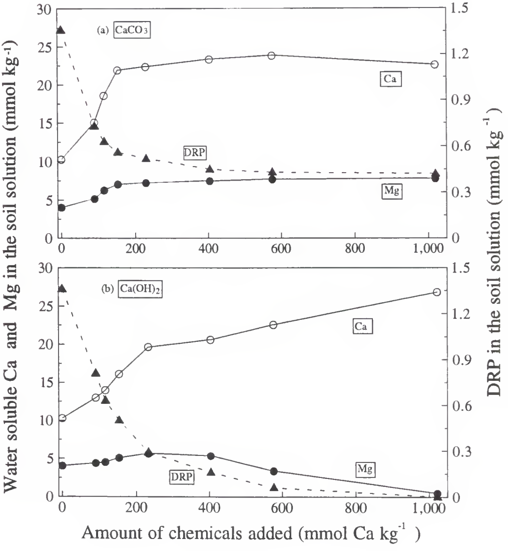

Fig. 2.7. Relationships among DRP, Ca, and Mg in the soil solution, as influenced by using $CaCO_3$ and $Ca(OH)_2$ amendments.

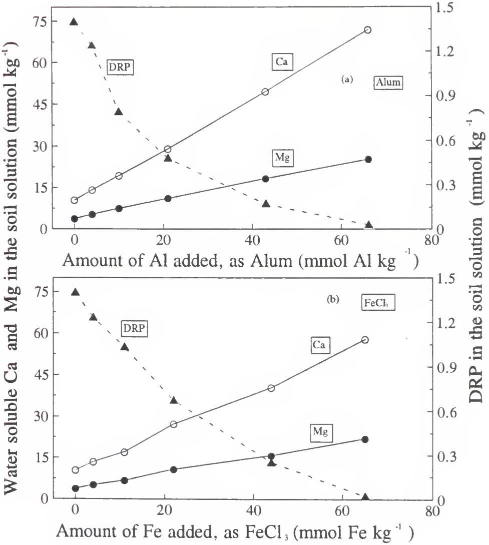

Fig. 2.8. Relationships among DRP, Ca, and Mg in the soil solution as influenced by using alum and FeCl$_3$

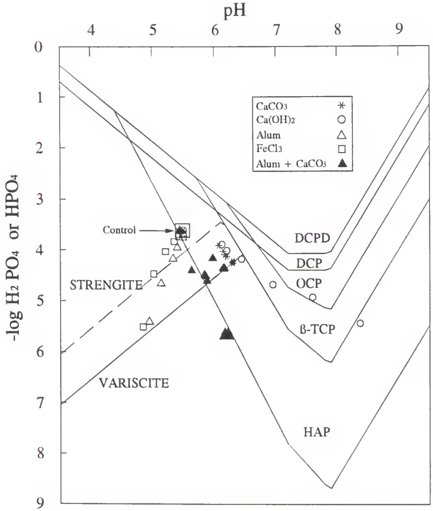

Fig. 2.9. Calculated solubility diagram of Ca, Al, and Fe phosphate minerals, and changes in the solubility of Ca, Al, and Fe phosphates in the soil solution as influenced by using various chemically amended soils.

and octa-calcium phosphate (OCP). In soils amended with $FeCl_3$ and alum, P solubility was controlled by amorphous P compounds of Fe and Al or partly strengite and variscite.

Discussion

Lime treatments

Addition of Ca salts to soil solution containing P causes the formation of a variety of Ca phosphates such as hydroxyapatite, dicalcium phosphate, beta tricalcium phosphate, octacalcium phosphate, calcium hydrogen phosphate, and calcium dihydrogen phosphate. The mechanisms regulating P retention in soils containing Ca, Mg, Al, and Fe are complex. Furthermore, P reactions would be more complicated in the soil solution if soil has high organic matter content. Hydrolysis of $CaCO_3$ in the soil solution results in the formation of OH^- and HCO_3^- ions, and as the OH^- ions are rapidly consumed by soil acidity, more carbonate ions may be released into the soil solution resulting in increased pH. The calcium ions released during hydrolysis may form surface P complexes and precipitate as amorphous Ca-phosphate compounds. The amorphous Ca-P compounds formed on solids, such as some soil particles and particularly the nucleus of crystalline calcite ($CaCO_3$), are gradually transformed into apatite, which is known to be most thermodynamically stable P compound (Stumm and Leckie, 1971). These processes can be interpreted as follows: 1) the formation of a stable primary crystalline nucleus, 2) the subsequent growth, and 3) the proliferation of the crystalline materials (Boskey and Posner, 1973). Although apatite is known to be the most thermodynamically stable P compound, it does not play a major role in controlling soluble P concentrations (Snoeyink and Jenkins 1980; Moore et al., 1990). The reason for this phenomenon has been explained by delayed crystal growth (Ferguson et al., 1970) and the presence of Mg (Marten et al., 1970), carbonate ions (Stumm et al., 1970), and organic acid (Inskeep et al., 1988; Reddy et al., 1990). A lack of calcite surface was also known to cause high P concentrations in water systems (Griffin et al., 1974; Kleiner, 1988). Calcium ions also may be combined with carbonate and phosphate ions to precipitate as calcium carbonate and calcium phosphate compounds, respectively. Laboratory studies using wastewaters showed that calcium carbonate precipitation was inhibited in solutions containing low carbonate ions at pH 9 due to orthophosphate. However, carbonate ions were competitive with phosphate ions in combining with calcium in the solution containing high carbonate ions (Ferguson et al.,1973). Phosphorus coprecipitation with carbonate ions may cause a rapid immobilization of soluble P at pH >9.2 (Otsuki and Wetzel, 1974).

Addition of $CaCO_3$ at a rate of 102 g kg^{-1} retained about 70% of water-soluble P, while a 100% reduction was obtained with the $Ca(OH)_2$-amended soil at the rate of 75 g kg^{-1}. Water-soluble P reduction increased up to 60% and 80% almost linearly with soil amended with $CaCO_3$ applied at 15.2 g kg^{-1} and $Ca(OH)_2$ at 17.3 g kg^{-1}, respectively (Fig. 2.5 a, b). Changes in soil solution pH followed the changes in water- soluble P concentrations, indicating that pH probably was the major factor in water- soluble P reduction in chemically amended soils. Soils amended with $CaCO_3$ and $Ca(OH)_2$ increased soil solution pH from 5.5 (unamended soil) to 6.3 and 9.7, respectively. Apparently, high pH values resulting from $Ca(OH)_2$ treatment were more efficient than $CaCO_3$ in reducing water-soluble P. A number of researchers have reported the effect of pH (Cole et al., 1953; Ferguson et al., 1970; Peterson et al., 1976; Ferguson et al., 1973; Babin et al., 1989). Calcium phosphate precipitation was found to be slower in wastewaters with pH < 9 and rapid in wastewaters having a pH above 10 (Ferguson et al., 1970). The pattern in Ca solubility changes was shown to be identical to that in pH changes resulting from $CaCO_3$ and $Ca(OH_2)$ treatments.

Generally, dissolved inorganic carbonate ions are known to compete with orthophosphate ions to precipitate calcium carbonate (Ferguson, 1970). However, the solution containing a low carbonate concentration (3.3 mM) lowered the P concentration to 0.01 mM, while carbonate concentration higher than 3.3 mM inhibited Ca-P precipitation (Ferguson, 1969). Similarly, the study also showed that $CaCO_3$ precipitation was inhibited with a low orthophosphate concentration in the solution containing low carbonate ions. It may be explained that most phosphate ions are adsorbed or precipitated with calcium ions before carbonate ions can combine with Ca (Lawrence et al., 1969). Dissolved inorganic carbon (DIC) concentrations in soil solutions were increased with $CaCO_3$ treatments, and the concentration decreased sharply at a pH of about 8.35 in $Ca(OH)_2$ treatments (Fig. 2.4 a, b). The decrease in DIC concentrations may indicate that calcium carbonate began to precipitate at around a pH 8.35. This trend was further supported by the decreased soil solution calcium concentration (Fig. 2.3 b), suggesting that more P was retained by the $Ca(OH)_2$ treatments than by $CaCO_3$ treatments as a result of coprecipitation with newly formed calcium carbonate. Babin (1989) also reported that $Ca(OH)_2$ was more effective than $CaCO_3$ in reducing total P concentrations in storm water.

Alum/$FeCl_3$ Treatments.

When alum is added to a solution, Al ions interact with water molecules to form hydroxo-complexes and a solid form of $Al(OH)_3(s)$ through a series of hydrolysis reactions (Cooke et al., 1981). Only a small portion of Al ions can be present in the forms of free Al^{3+}, and the balance of the Al ions are known to be in the hydroxide forms (Hsu, 1964). Therefore, $AlPO_4(s)$ precipitation may be minimal through the reaction of Al^{3+} with phosphate. Most of the Al-bound P precipitation is regarded as linkages, such as Al-OH-Al and Al-PO_4-Al in conjunction with organic acids (Hsu, 1976).

Alum and $FeCl_3$ also were effective in reducing water-soluble P concentrations. When alum was applied at a 21.8 g kg^{-1} , water-soluble P decreased from 44 mg P kg^{-1} soil to 1 mg P kg^{-1} soil in three days (Table 2.4). To remove about 80% of water-soluble P, 12.5 g kg^{-1} soil of alum was required (Fig. 2.5 c). Also, the highest rate of alum treatment decreased the pH to less than 5 from the initial pH 5.5, indicating that the soil had a high pH buffering capacity. Alum generally is not recommended as an amendment unless the soils are limed because of the potential problems associated with soil acidity and Al toxicity (Yuan et al., 1989). However, alum has long been used as a coagulant in wastewater treatment (Ferguson et al., 1977) and also is suggested for P control in P-enriched surface water (Cooke et al., 1978; Kennedy et al., 1982).

Ferric iron salts have long been considered as precipitants for P removal from wastewater systems (Sanville et al., 1976). Iron metals are hydrated in the solution first. The hydrated iron donates protons to a solvent water molecule, resulting in the formation of OH^- ions from the coordinated water molecule and a decrease in pH and alkalinity of the ambient water (Stumm and Morgan, 1962). Like Al ions, only 20% of the Fe added to solution can be present as free Fe and the balance is present as 40% of $Fe(OH)_2$, 5% of $Fe(OH)^{2+}$, and 35% of $(Fe_2(OH)_2)^{4+}$ (Stumm et al., 1962; Hsu, 1976). Thus, $FePO_4$ (s) precipitation is less expected than the $Fe(OH)_3$ formation in water solutions. Most of the P may be governed by the integrated particles in conjunction with iron hydroxyl compounds.

Application of $FeCl_3$ was found to be more effective than alum treatments in the reduction of water-soluble P. The soil solutions treated with $FeCl_3$ had a lower pH than soil solutions treated with alum. The hydrolyzing power of Al^{3+} was reported to be weaker than that of Fe^{3+} (Hsu, 1976). Also, Hsu reported that Fe^{3+} was more effective than Al^{3+} in P precipitation because Fe^{3+} has stronger affinity for phosphate and hydrolyzing power than Al^{3+}. It may be explained that the greater hydrolyzing power of Fe^{3+} causes decreased available free Fe ions (Snoeyink and Jenkins, 1980). Humic substances may be complexed with some cations such as Ca, Al, and Fe that sometimes combine with ligands such as carboxylic acid and orthophosphate ions. A molar ratio of 33 for Al (Fe) to P was required to remove 98% of water-soluble P in alum and $FeCl_3$ treatments. Such a high molar ratio ([Al] or [Fe]: P) may explain that in organic soils Fe and Al oxides are complexed with organic compounds. The molar ratio of Al to P for removing water-soluble P in lake water was reported to be 5 (Cooke and Kennedy, 1978). It was recognized that twice as much as Al salt was required for phosphate precipitation at pH 6 because $Al(OH)_3$ was expected to be precipitated in wastewater treatment (Snoeyink and Jenkins, 1980). The use of alum has not been recommended in acidic soils with a low buffering capacity because of Al toxicity. The soil used in this experiment was shown to be very stable in pH (around 5.5), which is ideal for Al-PO_4 precipitation (Ferguson, 1977).

Iron added as $FeCl_3$ was assumed to be dissociated and stayed as Fe^{3+} ion in the oxidized conditiuons since incubation was conducted under aerobic conditions. Dissolved Fe concentrations in soil solutions was less than 0.01 mg L^{-1}, suggesting that added Fe salt was dissociated, hydrolyzed, and stayed as solid forms of iron complexes. These solid forms of iron compounds may be removed by the filtering processes (Nealson and Saffarini, 1994). Therefore, fixation of phosphate by Al and Fe may be dependent on the activities of amorphous aluminum hydroxides and iron oxides rather than free Al^{3+} and Fe^{3+} (Hsu, 1965).

From the mixtures of alum/$CaCO_3$, alum hydrolysis can result in the release of free Ca ions from $CaCO_3$ and the formation of OH^- and HCO_3^- ions. The OH^- ion is associated with H^+, which is produced from the hydrolysis of the aluminum-hydroxo complexes. The solubility of $CaCO_3$ may be increased through this process (Yuan, 1981). As a result, increasing numbers of reactive sites, such as Al hydroxides and $CaHCO_3$, and Ca-Al complexes may be available for P retention. Also, there was some possibility of discrete P precipitation with free Ca and Al.

The ion activity product (IAP) calculated from P minerals (Table 2.6) showed that unamended soil (control) was supersaturated with respect to hydroxyapatite, variscite, strengite, $AlPO_4$, $FePO_4$, and wavellite. The amended soil treated with $CaCO_3$ was

Table 2.6. Average pK values of selected phosphate minerals in chemically amended Lake Apopka marsh soil solutions.

Amendments	Control	$CaCO_3$	$Ca(OH)_2$	Alum	$FeCl_3$	$CaCO_3$/Alum
Minerals	$pIAP^M$ ± S.D	$pIAP^M$ ± S.D	$pIAP^M$ ± S.D	$pIAP^M$ ± S.D	$pIAP^M$ ± S.D	$pIAP^M$ ± S.D
Hydroxy-apatite (pK=119)	118.9 ± 0.33	109.4±0.90	104.8 ± 7.50	122 ± 2.95	124.2 ± 5.10	116 ± 0.81
$Ca_{10}(PO_4)_6(OH)_2$	(118.6-119.5)	(108-111)	(92.8-117)	(118-126)	(119.5-133.4)	(115-117.7)
Betatricalcium (pK=28.9)	33 ± 0.09	30.4 ± 0.23	29.6 ± 2.74	34.0 ± 0.95	34.7 ± 1.62	32.5 ± 0.21
ß-$Ca_3(PO_4)_2$	(32.9-33.2)	(30.1-31.0)	(26.4-35.5)	(32.9-35.4)	(33.2-37.6)	(32.4-32.8)
Octacalcium (pK=46.9)	53.6 ± 0.12	50.5 ± 0.24	50.4 ± 4.80	55.1 ± 1.34	55.9 ± 2.31	53.3 ± 0.22
$Ca_4H(PO_4)_3 2.5H_2O$	(53.4-53.7)	(50.0-51.0)	(46.7-61.8)	(53.5-57.1)	(53.8-60.1)	(53.1-53.7)
Dicalcium Phosphate	20.6 ± 0.03	20.1 ± 0.02	20.8 ± 2.24	21.0 ± 0.41	21.2 ± 0.69	20.8 ± 0.03
Dihydrate (pk=18.9)	(20.5-20.7)	(20 .1-20.1)	(19.1-26.3)	(20.6-21.6)	(20.6-22.5)	(20.8-20.8)
$CaHPO_4 2H_2O$						
Variscite (pK= 22.1)	18.5 ± 0.19	19.6± 0.28	23.6 ± 5.80	19.5 ± 0.51	19.8 ± 0.95	19.7 ± 0.09
$AlPO_4$ (pK=19.1)	18.5 ± 0.19	19.6± 0.28	23.6 ± 5.80	19.5 ± 0.51	19.8 ± 0.95	19.7 ± 0.09
	(18.3-18.8)	(19.2-20.0)	(18.1-36.3)	(18.7-20.2)	(18.9-21.5)	(19.5-19.8)
Strengite (pK =264)	24.3 ± 0.30	27.5 ± 0.76	29.9 ± 4.90	24.4 ± 0.09	24.3 + 0.46	27.04 ± 0.5
$FePO_4$ (pK = 25.9)	24.3 ± 0.30	27.5 ± 0.76	29.9 ± 4.90	24.4 ± 0.09	24.3 ± 0.46	27.04 ± 0.5
	(23.9 ± 24.7)	(26.2-28.6)	(24.5-39.5)	(24.2-24.5)	(24.1-25.2)	(26.4-27.2)
Wavellite (pK = 73.6)	68.9 ± 0.59	71.1 ± 0.7	79.9 ± 12.8	71.3 ± 1.26	72.5 ± 2.40	71.2 ± 0.12
$Al_3(PO_4)_2(OH)_3 5H_2O$	(68.3-69.7)	(70.1-72.0)	(67.7-107)	(69.6-73.2)	(70.1-76.7)	(71.1-71.4)
Whitlockite (pK = 222)	248.8 ± 0.87	236 ± 0.75	236.6±22.6	255 ± 5.82	259 ±10.6	249 ± 0.91
$Ca_{18}(Fe,Mg)H_2(PO_4)_{14}$	(247-250)	(235-238)	(220-290)	(248-263)	(249-278)	(248-250)

supersaturated with respect to variscite, $AlPO_4$, wavellite, and hydroxyapatite. The amended soil treated with $Ca(OH)_2$ was supersaturated with respect to only hydroxyapatite. However, the ranges of calculated pIAP values clearly indicated that $Ca(OH)_2$ amendment could be in equilibrium or supersaturated with respect to β-tricalcium and octacalcium phosphates, although the calculated mean values of pIAP for β-tricalcium and octacalcium phosphates were shown to be larger than the pK values, which suggests undersaturation with respect to Ca-P compounds (Table 2.6). Soils amended with alum and $FeCl_3$ wereundersaturated with respect to hydroxyapatite and supersaturated with respect to variscite, strengite, $AlPO_4$, $FeCl_3$, and wavellite. The mixture of $CaCO_3$ and alum also was supersaturated with respect to hydroxyapatite. Amended soils except for $Ca(OH)_2$ amendment were shown to be undersaturated with respect to dicalcium phosphate and whitlockite (Table 2.6).

The calculated pIAP values and solubility diagrams of Al/Fe P minerals showed Al and Fe were controlling the DRP concentrations in the Lake Apopka marsh soil. In particular, soils were shown to be more saturated with respect to amorphous $AlPO_4$ and $FePO_4$ than variscite and strengite. Wang et al. (1991) provided evidence that amorphous ferric phosphate was formed in Floridian phosphatic soils. Olila et al. (1994) were unable to detect any crystalline P minerals in Lake Okeechobee sediments using X-ray diffraction, suggesting that this was due to the amorphous nature of P compounds rather than crystalline P minerals. Also, the solubility diagram and pIAP indicated that this soil was supersaturated with respect to Ca-bound P, especially hydroxyapatite. Apatite precipitation is unlikely since its formation may be hindered by the presence of Mg

(Marten and Harris, 1970), carbonate (Stumm and Leckie, 1970), and organic acids (Inskeep and Silvertooth, 1988). Calcium P solubility in these soils may be dependent upon the calcium complexes binding P and calcite, which is known to be coprecipitated with P. These mechanisms are recognized as sorption rather than precipitation. To determine which carbonate minerals control P concentrations in the unamended soil, the IAP of three carbonate minerals were determined (Table 2.7). These data showed that only $Ca(OH)_2$ amended soil was supersaturated with respect to calcite, indicating that P coprecipitation with CO_3^{2-} on the nucleus of the calcite (Otsuki and Wetzel, 1972). This result was well balanced with the data regarding pH and the concentrations of DIC and Ca in floodwater treated with $Ca(OH)_2$ as mentioned in the previous sections.

In a calculation of lime required to raise the soil pH, only soils amended with calcium hydroxide could increase the soil pH higher than 7. To increase the pH by 1 unit in Lake Apopka marsh soil, about 5 metric tones of $Ca(OH)_2$ per hectare was required (Fig. 2.10). All chemical amendments, except $CaCO_3$ showed a high coefficient of determination (R^2) between amount of chemical amendments and the soil pH.

Conclusions

Unamended soil released 1. 4 to 1.6 mmol P kg^{-1} soil to the soil solution during the incubation period, suggesting that accumulated P in this soil is highly water soluble. All amended soils ($CaCO_3$, $Ca(OH)_2$, alum, and $FeCl_3$) potentially were effective in decreasing water-soluble P concentrations. The effective rates required for each amended soil to minimize P release into soil solution were 15 to 23 g kg^{-1} soil and 17 to 30 g kg^{-1} for $CaCO_3$ and $Ca(OH)_2$, respectively. Up to a 62% reduction in water-soluble P can be

Table 2.7. Mean pK values of selected carbonate minerals in the chemically amended Lake Apopka marsh soils used in the batch incubation study.

Chemical Amendments	Aragonite (pK=8.16)			Calcite (pK= 8.34)			Dolomite (pK=17)		
	$pIAP^M$	S.D	Range	$pIAP^M$	S.D	Range	$pIAP^M$	S.D	Range
Control	12.2	0.05	12.2-12.3	12.2	0.05	12.2-12.3	30.6	0.12	30.6-30.8
$CaCO_3$	9.5	0.27	9.2-12.3	9.5	0.27	9.2-12.3	24.7	0.63	24.0-25.8
$Ca(OH)_2$	8.3	1.40	6.1-10.1	8.3	1.40	6.1-10.1	22.0	0.55	29.3-31.0
$FeCl_3$	12.8	0.30	12.3-13.2	12.8	0.30	12.3-13.2	31.2	0.54	30.5-32.1
$CaCO_3$/Alum	9.8	0.32	9.2-10.3	9.8	0.32	9.2-10.3	24.9	0.63	23.5-26.1

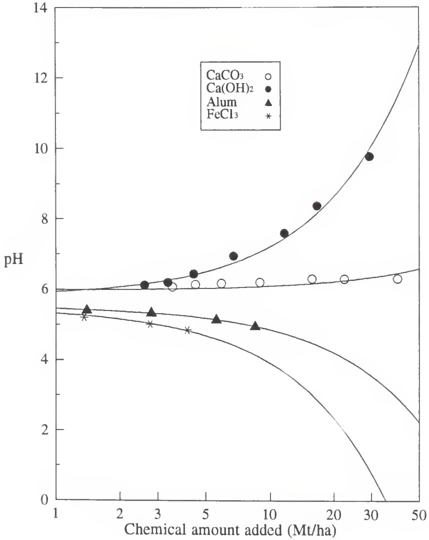

Fig. 2.10. Effects of various amounts of chemical amendments on soil pH. Each amount was calculated based on metric ton per hectare. Note log scale on the x-axis.

obtained from these rates for $CaCO_3$ treatment and a 79% reduction for $Ca(OH)_2$ treatment. To remove more than 80% of water-soluble P, alum and $FeCl_3$ treatments at rates higher than about 12.5 and 7.1 g kg^{-1} were required.

A phosphorus solubility diagram and IAP calculated based on equilibrium constants of P minerals showed that unamended soil was supersaturated with respect to hydroxyapatite, variscite, strengite, $AlPO_4$, $FeCl_3$, and wavellite. The soils amended with $CaCO_3$ was supersaturated with respect to hydroxyapatite as well as variscite, wavellite, and $AlPO_4$. The soils amended with alum and $FeCl_3$ were supersaturated with respect to variscite, strengite, $AlPO_4$, $FePO_4$, and wavellite. The calculated pIAP of carbonate minerals suggested that calcite may be formed in the soil amended with $Ca(OH)_2$, indicating coprecipitation of P with calcite. The results obtained from the pIAP and solubility diagram indicated that Al and Fe as well as Ca controlled water-soluble P concentrations in the constructed wetland. Although the solubility diagram showed that hydroxyapatite controlled water-soluble P in Lake Apopka marsh soil, more soluble Ca-bound P was expected to be formed because of high concentrations of Mg and a large amount of organic matter. The solubility diagram of Al- and Fe-bound P compounds of Lake Apopka marsh soil showed that amorphous $AlPO_4$ and $FeCl_3$ were probably formed in the soil instead of thermodynamically stable compounds such as variscite and strengite. Among the treatments studied, the soils amended with $Ca(OH)_2$ and $FeCl_3$ appeared to be promising amendments in immobilizing DRP by retaining P in the amended soils before releasing to the floodwater. Caution, however, should be exercised in using $FeCl_3$ and $Ca(OH)_2$ because of their sensitivity to changes of redox potential and pH, respectively.

CHAPTER 3
PHOSPHORUS FLUX FROM CHEMICALLY AMENDED LAKE APOPKA MARSH SOILS

Introduction

Phosphorus inputs to fresh water aquatic systems is attributed to agricultural runoff, domestic and industrial discharges, and precipitation (Petterson, et al., 1988). Control of these discharges by chemical treatment started 20 years ago and today it is a well-established technology (Balmer and Hultman, 1988).

Soils previously used for agriculture are currently being converted to marshes with the hope that these constructed marshes will function as sinks for nutrients. Such systems are created in areas adjacent to sensitive aquatic systems. Flooding previously fertilized agricultural land results in solubilization of residual fertilizer nutrients such as inorganic P and their release into the overlying water column (Reddy and D'Angelo, 1994). To reduce P flux from soils it may necessary to immobilize soluble P into nonavailable forms and reduce P flux into floodwater. This may be accomplished by adding chemical amendments containing Ca, Fe, or Al that bind P into insoluble forms. The addition of chemicals to inactivate/precipitate soluble P has long been used in advanced wastewater treatment (Ferguson and McCarty, 1971; Cooke and Kennedy, 1981) because of its efficiency in P removal and ease of application to wastewater (Balmer and Hultman, 1988). This technology was extended to restore excessively eutrophic lakes (Kennedy and Cooke, 1982) and immobilize contaminants in stormwater retention ponds (Babin, et al, 1992).

Phosphorus inactivation/precipitation in freshwater ecosystems is a procedure to remove P from the water column and to control its release from sediments. The advantages of P inactivation over other restoration methods are its relative ease of application, wide scope of applicability, and high potential for P inactivation, while it has the disadvantage of forming flocculent hydrous oxides which can be potentially resuspended by wave action and currents in shallow lakes (Sanville et al., 1976). Sedimentation on the top of sediments after applying chemicals may be one of the critical factors in reducing the effectiveness of P entrapment (Barko et al., 1990).

The addition of Ca amendments can result in the formation of a variety of insoluble phosphate compounds. The formation of calcium phosphate compounds closely is related to the concentrations of Mg (Martens and Harris, 1970), carbonate ions (Stumm and Leckie, 1970), organic acids (Sinha, 1971), and humic substances (Innskeep and Silvertooth, 1988), redox potential (Patricks, 1964; Reddy, 1990), and pH. In calcareous sediments, P inactivation is associated with calcium carbonate (Stumm and Leckie, 1970), while in noncalcareous soils it is controlled by the solid phases containing Fe and Al (Hsu, 1964).

Aluminum has been used most often in P immobilization studies because Al complexes and polymers are relatively insensitive to redox changes and effective in the entrapment of inorganic and particulate P (Cooke et al., 1977). When Al salt is added to a solution, Al ions are hydrated due to the polarity of water molecules and then hydrolyzed in series forming polymeric hydroxy-aluminum complexes or aluminum hydroxides, oxides, and oxyhydroxides, resulting in decreased pH and alkalinity (Snoeyink and Jenkins, 1980). The activity of Al^{3+} in solution is limited by pH, being negligible at pH 5 and above, while there is no limitation of the reactivities of amorphous aluminum hydroxides (Hsu, 1964). Therefore, the effectiveness of aluminum phosphate ($AlPO_4$) precipitation is related to the initial molar ratio ([P]/[Al]) in solution (Hsu, 1975). Phosphorus can be completely removed from the solution if sufficient Al is present. At maximum, 1 mole of P is precipitated by 1 mole of Al, but this occurs only when P is in excess, assuming that Al-OH-Al and Al-PO_4-Al linkages are integrated in the reaction products (Hsu, 1975, 1976; Diamadopoulos and Benedek, 1984). The ratios of Al to PO_4 for wastewater and freshwater ecosystem treatments were reported to be 2 (Snoeyink and Jenkins,1980) and 4 to 7.2, (Jenkins et al, 1971; Peterson, et al, 1976), respectively. Phosphorus is removed by entrapment of particulates and precipitation of $AlPO_4$ (Recht and Ghassemi, 1970).

Phosphorus precipitation and sorption are influenced by pH and P concentration (Stumm and Morgan, 1981). Aluminum phosphate ($AlPO_4$) may be the predominant reaction product in a wastewater which usually contains high P concentration and low pH, which results in high available Al^{3+}. Eutrophic lakes, however, can be characteristically alkaline and P concentrations relatively low (Cooke et al., 1982). At a higher pH and low P concentrations, OH^- reacts more readily with Al rather than with P. The relative affinity of various ions to coordinate with Al is suggested as follows: $OH^- > F^- > PO_4^{-3} > SO_4^{2-} > Cl^- > NO_3^-$ (Diamadopoulos and Benedek, 1984). Therefore, aluminum hydroxide may be more responsible for adsorbing P rather than forming a discrete $AlPO_4$ for freshwater ecosystems. Although the reactions of Fe salts with P follow a similar trend as Al salts with P, the effectiveness and acidity are different.

Minimum solubility is predicted to be one order higher of magnitude than Al, and it is likely to occur at about pH 5, which is one unit lower than Al (Jenkins et al., 1971). Iron (Fe^{3+}) is able to hydrolyze and polymerize spontaneously and rapidly to $Fe(OH)_3$ (Hsu, 1973). Hsu (1973) explained that only 20% of Fe was able to be Fe^{3+}, and an excess of Fe was converted to forms of iron hydroxide. Hsu (1976) reported that Fe^{3+} has a stronger affinity for P and stronger hydrolyzing power than Al^{3+} in the comparing two experiments conducted using Fe (1973) and Al (1975). However, Fe^{3+} is sensitive to redox changes and is expected to reduce to Fe^{2+} under anaerobic conditions. Thus, P is believed to be released to the ambient water during the reducing period.

The addition of alum and ferric chloride to the soil decreases the pH of the system. Hydrolysis is responsible for low pH. Application of Al salts or Fe salts to the system for phosphate removal results in the precipitation of aluminum hydroxyphosphate ($Al_x[OH]_y[PO4]_z$) and ferric hydroxyphosphate ($Fe_x[OH]_y[PO4]_z$). Also, aluminum phosphate and ferric phosphate in discrete forms may be precipitated at a lower pH. However, under anaerobic conditions, ferric phosphate and hydroxyphosphate compounds are dissolved due to the reduction of Fe^{3+} to Fe^{2+}, and ortho-phosphate ions are released into the water column. Reduced irons may be competitive with orthophosphate, hydroxy, and carbonate ions. Combined applications of alum with $CaCO_3$ to the soil may have the advantage of controlling pH in the neutral range. It may be essential to apply the mixed chemicals to the water systems having a low pH buffering capacity.

Lake Apopka marsh soil contains several times higher concentrations of Ca than those of Fe and Al. The soil pH is in the range of 5.5-5.8. It also was likely that the soil was highly buffered in pH as a result of carbonate dissolution from the marl layer of the bottom soil below the organic soil. It was hypothesized that Fe and Al in the soil can play the role of controlling inorganic P because of its ideal soil pH. Phosphorus adsorption in this soil may be a more dominant mechanism than precipitation. It also was expected that amorphous calcium P compounds probably were precipitated in soil solutions treated with calcium materials because of their high capability to raise soil pH. Hydroxyapatite, which is the most stable P compound thermodynamically, may be formed slowly on the surface of the amorphous phosphorus compounds and other solid surfaces such as a calcite forming or already existing in the systems. However, the formation of hydroxyapatite and calcite may be hindered by high Mg and organic acid concentrations in the systems (Inskeep and Silvertooth, 1988).

From the bio-geo-physico-chemical characteristics described in the previous study (see Chapter 2) of the constructed wetland, some assumptions were made that Ca-, Al-, and Fe-bound phosphate compounds coexisted, and thus P solubility was controlled by three metal ions simultaneously in this wetland soil.

The main objective of this study was to evaluate techniques for immobilizing soluble P into nonavailable forms. The specific objectives were to 1) determine the effects of various chemical amendments on P flux between the soil and floodwater, 2) study P distribution in chemically amended soils, and 3) evaluate the solubility of P in chemically amended soils and its relation to soil physico-chemical properties. To accomplish these goals, two batch incubation experiments were conducted under laboratory conditions: 1) chemical amendments were incorporated with the whole soil column (Column study 1), and 2) chemical amendments were applied to the top 3 cm of the soil column (Column study 2).

Materials and Methods

Soil Sampling

Bulk soil was obtained from Station 5 (Fig. 3.1), located 3000 m from the inflow of the marsh created adjacent to the Lake Apopka. The wet soil was spread on a drying bed in a greenhouse equipped with fans for ventilation. The soil was mixed thoroughly, homogenized, and passed through a 10-mesh sieve, and lumps of soil were broken and detrital plant tissue was removed. Predetermined amounts of air-dried soils were transferred into vinyl bags and stored at 4°C until used in experiments. Overlying water collected from the field site was filtered to remove organic matter. The filtered water was mixed homogeneously in a large plastic water tank and stored in the dark under laboratory conditions (25° C).

Soil Characterization

Soil pH, water content, and organic matter content. Soil pH (1:1) was measured by using a glass electrode and pH meter. Organic matter was estimated by combusting a known amount of each air-dried sample in the furnace at 550°C for five hours (APHA, 1985). The loss in weight after combustion was calculated and expressed as percent volatile solids. Water contents of both fresh and air-dried samples were determined by oven-drying at 80°C for 72 hours or until a constant weight was recorded.

Water-soluble P and selected cations. A 0.2 g air-dried soil plus 20 ml distilled

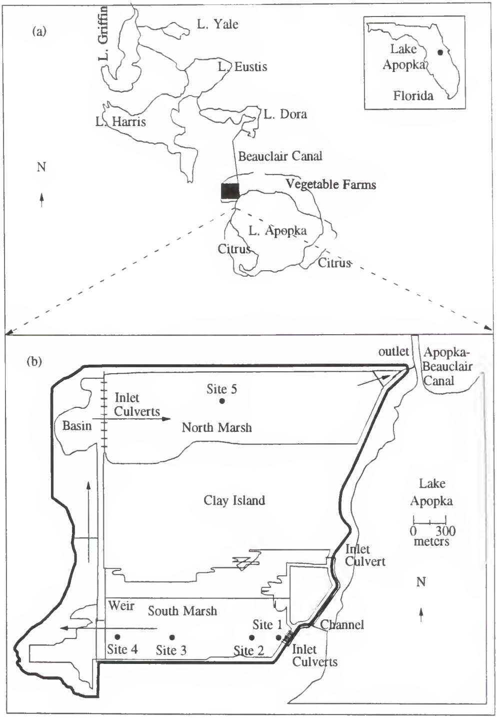

Fig. 3.1. (a) Oklawaha river basin, (b) A created marsh adjacent to Lake Apopka. Soil was obtained from Site 5 (north marsh).

and deionized (DDI) water was placed in 50 ml centrifuge tubes, shaken for 15 min, and centrifuged for 15 min at 6,000 rpm. The supernatant liquid was filtered through a 0.45 μm membrane filter. The residue was weighed and saved for the succeeding extractions. A total of six extractions with DDI water were performed sequentially on each sample. The solution was analyzed for dissolved reactive P (DRP) using standard methods (APHA, 1985). The concentrations of Ca, Mg, Al, and Fe in the extracts also were determined using atomic absorption spectroscopy.

HCl-extractable P and metal ions. A 0.2 g air-dried soil sample was treated with 20 ml of 1M HCl and shaken for three hours, followed by filtration through a 0.45 μm membrane filter. The extracts were analyzed for DRP and selected cations as described above.

Total P and metal ions. A 0.4 g air-dried soil sample was combusted in the furnace at 550°C for five hours (APHA, 1985). The combusted sample was treated with 20 ml of 6 M HCl solution and dried on a hot plate at a low temperature. After the sample beaker had cooled, 2.25 ml of 6 M HCl solution was transferred into the beaker and heated until just before boiling (Anderson, 1976). The sample was filtered through a No. 41 Whatman filter and diluted to 50 ml with DDI water. The extract was analyzed for total P using autoanalyzer, and cations were determined using atomic absorption spectroscopy.

Soil redox potential. A known amount of air-dried soil (20 g), mixed homogeneously with various chemicals ($CaCO_3$, $FeCl_3$, and alum), were transferred into the redox intensity tubes equipped with the platinum electrode, followed by flooding with filtered marsh water. The initial redox potential was not measured until the whole soil in the tube was soaked completely. Redox potential (Eh) was measured for several weeks with a Eh meter equipped with a pH electrode.

Experimental Set-Up

Previous batch incubation studies (Chapter 2) have shown that Lake Apopka marsh soil is a high potential source of P, and its release to the ambient water can be prevented by treating the soil with selected inorganic chemicals. The objectives of this study were to 1) determine the exchange of P between soil and overlying water column for various chemical treatments, and 2) evaluate two methods of chemical application: a) chemical application incorporated with whole soil in a column (Column study 1), and b) chemical application to the top 3 cm of the soil column (Column study 2). The amount of each chemical treatment for these column studies was determined on the basis of results obtained from previous batch incubation studies (see Chapter 2).

Column study 1. A known amount of air-dried soil (141g) was mixed with the chemicals at precalculated rates and placed in a plastic bag. The mixture was transferred into a Plexiglas column (I.D.=5 cm) stoppered at the bottom and packed according to field bulk density (0.26 to 0.28 g cm^3). The soil was flooded carefully with the filtered marsh water to obtain a floodwater depth of 10 cm. The initial height of the water and soil column was marked to check for any changes in depths at every sampling time. Each treatment consisted of three replication. The amount of various chemical amendments used is summarized as follows:

1) $CaCO_3$: (0, 9.0, 15.3, 40 and 102 g kg^{-1} of soil)

2) $Ca(OH)_2$: (0, 6.7, 11.3, 30, and 75 g kg^{-1} of soil)

3) $CaMg(CO_3)_2$: (0, 14.7, 25.4, 67, and 170 kg^{-1} of soil)

4) Alum: (0, 3.7, 7.1, 14.5, and 23 g kg^{-1} of soil)

5) $FeCl_3$: (0, 1.8, 3.5, 7.1, and 11.5 g kg^{-1} of soil)

6) $CaCO_3+Ca(OH)_2$ (0, 4.5+3.34, 7.6+5.7, 20.2+15.1, and 51+38 g kg^{-1} of soil)

7) $CaCO_3$+alum (0, 4.5+1.9, 7.6+3.8, 20.2+7.3, and 51+11.6 g kg^{-1} of soil)

8) $CaCO_3+FeCl_3$ (0, 4.5+0.92, 7.6+1.8, 20.2+3.5, and 51+5.8 g kg^{-1} of soil)

On an areal basis (bulk density of soil = 0.281 g cm^{-3} and 20 cm soil depth), 1 g kg^{-1} of amendment will equal to 56 g m^{-2}. Treatments 6), 7), and 8) were based on equal proportions of respective chemicals (1:1 ratio by weight) added at 50% of their individual treatment rates. Each treatment was replicated three times.

Column study 2. Air-dried soil (111 g) was packed into a Plexiglas column, and then the chemically amended soils (30 g air-dried soil mixed with precalculated chemicals) were added to a top soil (3 replications per treatment). The soil column was flooded slowly with the filtered lake water to obtain a floodwater depth of 10 cm. Immediately after flooding, the pH and electrical conductivity (EC) of the floodwater were measured. The columns were incubated in the dark at 25° C with periodic measurements of pH and EC. The depth of the water column was maintained by adding deionized water to replace water lost due to evaporation.

Experimental Procedures

Water and soil sampling. Fifty milliliters of the floodwater sample was removed once a week for soluble P analysis. The amount of floodwater removed was replaced with filtered (0.45 μm) marsh water. At each sampling period, about 25% of the floodwater was replaced, with complete turnover in 4 weeks. This procedure was repeated for a total of three 4-week cycles. Water samples obtained at weekly intervals were filtered through 0.45 μm membrane filters and analyzed for DRP using standard methods (APHA, 1985). Water samples taken after every 4 week were also be analyzed for inorganic carbon (IC), TP, Ca, Mg, Fe, Al, Na, K, Mn, Zn, and Cl. Electrical conductivity (EC) and pH of the floodwater were measured once a week.

The column experiments were terminated after 12 weeks of incubation. The floodwater column was removed and analyzed as previously described. The soil columns were extruded and sectioned into 0-3 and 3-14 cm depth increments under anaerobic conditions. The porewater was extracted by centrifugation at 6000 rpm for 15 min. The supernatant was filtered through a 0.45 μm membrane filter and analyzed for SRP, IC, Cl, and cations (Ca, Mg, Al, Fe, Na, K, Zn, Mn). The residual soil after porewater removal was fractionated into labile and nonlabile pools using an inorganic P fractionation scheme similar to that of Hieltjes and Lijklema (1980). Predetermined residual samples (0.5 g) were shaken for two hours with 20 ml of DDI water. Subsequently, the extracts were centrifuged and filtered as above. The residual soil was then shaken for 17 h with 0.1 M NaOH for assessment of non-apatite P, centrifuged, and the supernatant filtered. The residual soil was then extracted for 24 h with 0.5 M HCl to obtain an estimate of apatite P. All fractionation steps were conducted under anaerobic conditions.

Phosphorus flux calculation. Phosphorus flux within the columns during the first week was determined as follows:

Flux (μg) = $(V_1 * C_1) - (V_0 * C_0)$
where:
V_1 is floodwater volume at the end of first week,
C_1 is DRP concentration in floodwater at the end of first week,
V_0 is floodwater volume on the first day of incubation, and
C_0 is initial DRP concentration of filtered Lake Apopka marsh water.

The general P flux equation after the first week of incubation was

$$[(V_i * C_i) - ((C_o * 50 \text{ ml}) + (V_{i-1} - 50 \text{ ml}) * C_{i-1})]$$

where:
V_i is floodwater volume at the end of i_{th} week.
C_i is SRP concentration in floodwater at the end of i_{th} week.
V_{i-1} is floodwater volume of previous week.
C_{i-1} is floodwater SRP concentration of previous week.

Inorganic P fractionation

KCl extractable P. Phosphorus extracted with 20 ml of 1 M KCl solutions (soil to solution ratio of 1:100) represents the readily desorbable pool of P. Soil solutions were equilibrated for a period of 1 h. by continuously shaking on a mechanical shaker, followed by centrifugation at 6,000 rpm for 15 min. Supernatant solution were decanted through a 0.45 μm membrane filter. The solution was analyzed for DRP. The residual soil sample was used in the following sequential extraction.

NaOH extractable P. The residual soil obtained from the above extraction was treated with 20 ml of 0.1 M NaOH. Soil suspensions were allowed to equilibrate for a period of 17 h by continuously shaking on a mechanical shaker, followed by centrifugation at 6,000 rpm for 15 min. Extraction with 0.1 M NaOH removes the P mainly associated with Al and Fe, and partly associated with fulvic and humic acid.

HCl extractable P. The residual soil obtained from the above extraction was treated with 20 ml of 0.5 M HCl. Soil solutions were allowed to equilibrate for a period of 24 h by continuously shaking on a mechanical shaker, followed by centrifugation at 6,000 rpm for 15 min. The filtered solutions were analyzed for DRP. This fraction P represents Ca-bound P.

Analytical Methods

Dissolved reactive phosphorus (DRP). Phosphorus in all extracts except that of KCl was determined by the ascorbic acid method (Murphy and Riley, 1962) using an autoanalyzer (Technicon AA II). Phosphorus determination in KCl extracts was slightly modified by heating the sample-reagent mixture to 60°C for 5 min on a hot plate (Folsom et al., 1977). The mixture was allowed to cool at room temperature, and the blue color was read at 880 nm using a Shimadzu (UV-160) spectrophotometer.

Total phosphorus (TP). Total P was determined by the ignition method (Saunders and Williams, 1955). Air-dried soil samples were oven-dried (90°C). Four hundred milligrams (oven-dried weight) of each soil sample was weighed into a 50 ml beaker and heated to 200°C in a muffle furnace for 30 min. Then, the temperature was increased to 550°C. After 4 hours, the samples were allowed to cool down to 200°C and removed from the furnace. Each sample was moistened with distilled water, 20 ml of 6 M HCl was added, and the mixtures were slowly digested to dryness on a hot plate at a low temperature. Each residue was dissolved in 2.5 ml 6 M HCl near the boiling point and filtered (Whatman #41). Each filtrate was diluted to a 50 ml volume and stored at 4° C until analyzed for P (Murphy and Riley, 1962). This procedure also was used to determine 0.1 M NaOH-resistant organic P. Five milliliters of each homogenized extract was transferred to a preweighed 50 ml beaker and allowed to dry in the oven at $40^{\circ}C$. Then, the temperature was increased to 80° C. The dried samples were weighed and analyzed for TP by the ignition method (Saunders and Williams, 1955).

Metals. The soils were analyzed for water-soluble and 1M HCl extractable Ca, Mg, Al, and Fe. Total metals were determined by the ignition method. The metals were analyzed using an inductively coupled argon plasma (Thermo Jarrell Ash ICAP 61E; Franklin, MA).

Other analyses. Electrical conductivity was measured using a conductivity meter (YSI Model 31) and inorganic carbon was analyzed by TOC analyzer (DC-190 ASM, Dohrmann).

Mineral Equilibria.

The computer program SOILCHEM (Sposito and Coves, 1991) was used to predict chemical speciation of P in the liquid phase. Input consisted of the measured concentrations of Al, Ca, Fe, K, Na, Mn, Mg, Zn, P, water-soluble inorganic carbonate, and Cl, and pH levels. Activity coefficients were calculated using Davies equation and ionic strength values calculated by SOILCHEM. When calculating ion activities, precipitation was not assumed to occur.

P Mineralogical Analysis.

Air-dried amended soils (10 g) obtained from the incubation study were treated with about 2 L of sodium hypochlorite (NaOCl) and incubated for a day to remove organic matter. The samples were washed with 1 N NaCl to saturate then with Na and filtered through a 50 μm mesh sieve to separate sand from silt and clay. The sand fractions were air-dried and stored in small labeled nalgene bottles. Silt and clay were separated by centrifugation. Glass slides for clay mounts were prepared by transferring the clay collected on 0.45 μm filter paper onto the slides. Silt and sand were ground to be mounted on ceramic tiles. X-ray diffraction (XRD) analysis was performed using a computer-controlled XRD system. The mounts were scanned at 2 θ per min with CuKα radiation at 35 kV and 20 mA.

Results

Physico-Chemical Properties of Soils

Selected chemical characteristics of the soil (Site 5) used in the study are shown in Table 3.1. Total inorganic P as determined by 1 M HCl extraction represented up to 42% of the total P. About 3.5% of the total P (8.4% of the total inorganic P) was in water-extractable fraction. One M HCl extractable P was charged of 42% of the total P. Surface water pH of the Lake Apopka marsh was 6.5, whereas soil pH of air-dried soils (1:1) was 5.5 to 5.8.

Calcium and Mg are the dominating cations in the Lake Apopka marsh soil. About 0.9% and 2.1% of 1 M HCl extractable Ca and Mg, respectively, were shown to be water soluble, indicating that Mg is more soluble than Ca in this slightly acidic soil solution. Aluminum and Fe were hardly detected in the DDI water extraction or the surface water, indicating that the activities of Al^{3+} and Fe^{3+} may be limited in the slightly acidic to neutral solution (Hsu, 1964). Another reason may be that most crystalline forms of Al and Fe probably were not filtered through a 0.45 μm membrane

Table 3.1. Some physico-chemical properties of water and soil samples obtained from Site 5 of Lake Apopka Marsh Flow-way Demonstration Project.

Properties			Water Sample	Soil Sample
Bulk density		(g cm^{-3})		0.28
Water content		(g kg^{-1})		830
pH			6.5	5.55
Ec		(mS m^{-1})	31	
Dissolved Reactive	P	(mM)	0.01	
Dissolved	Ca		0.88	
	Mg		0.79	
	Fe		0.001	
Water Extractable	P	(mmol kg^{-1})		0.71
	Ca			8.8
	Mg			3.2
	Fe			0.24
1 M HCl extractable	P	(mmol kg^{-1})		8.5
	Ca			954
	Mg			156
	Fe			64
	Al			33
Total	P	(mmol kg^{-1})		20
	Ca			970
	Mg			159
	Fe			100
	Al			106

filter because of their solid forms in aerobic conditions (Nealson and Saffarini, 1994). Minimum solubility of Al and Fe was shown to be at pH 6 and 5.4, respectively. (Snoeyink and Jenkins, 1980). Aged and/or newly formed Al hydroxides, Fe oxides, and complexes formed with organic matter were regarded as main factors for the low solubility of Al and Fe in this slightly acidic condition (pH 5.5 to 6). Surface reactivities of such Al hydroxide and Fe oxides may play an important role in fixing P (Hsu, 1975). Therefore, the P fixation by Al and Fe salts may be dependent on the activities of amorphous aluminum hydroxides and Fe oxides rather than free Al^{3+} and Fe^{3+} (Hsu, 1965).

The mole ratio of total Ca to Mg was 6:1, whereas the ratio of total Fe to Al was 1.6:1in the soil sample. The mole ratios of water-soluble Ca to Mg were 1.1:1 and 2.8:1 in the surface water of the Lake Apopka marsh and DDI water extracts, respectively. Such low ratios in the surface water and DDI water extracts may indicate some competition between Mg and Ca to combine with P (Martens and Harriss, 1970). Under oxidized conditions the solubility of Ca was reported to be almost identical to that of Mg. However, Mg is more soluble than Ca in the slightly acidic solution (Reddy and Graetz, 1990).

From these initial soil characteristics, it was assumed that high P flux between floodwater and soil was occurring in this soil, and amorphous Ca- and Fe-bound P probably are major factors in controlling inorganic P in this soil. The soil P fractionation study showed that Ca-bound P (0.5 M HCl extractable) dominated within 20 cm of soil depth, while in deeper soil than 20cm, Al- and Fe-bound P (0.1M NaOH extractable) was more than Ca-bound P (Reddy and D'Angelo, 1994). The bulk of the soil used for this incubation study was obtained from the surface 25 cm depth. Soil pH was 5.8, whereas pH of the marsh water was 6.5. The slightly acidic soil may have been related to the accumulation of carbon dioxide and organic acid produced during decomposition of organic matter and hydrolysis of Al and Fe.

Redox Intensity of Amendment Soils

The patterns of redox potential (Eh) change were all similar to each other in the floodwaters of both chemically amended and unamended soil. There was no evidence that chemically amended soils affected the Eh in the floodwater. Redox potential in the floodwater of the unamended soil (Control) was maintained in the range of 250 to 350 mV (Fig. 3.2 a), and Eh was well poised at about 350 mV for all chemically amended soils. During the initial 7 days, the Eh of the top 3 cm of the soil column for control was decreased from 400 to 200 mV, and then reduced gradually to 150 mV (Fig. 3.2 a). It took a few days to get 250 mV from 300 mV in the top 3 cm of the soil column treated with $CaCO_3$, and then the Eh was well maintained above 200 mV during the incubation period (Fig. 3.2 b). The initial Eh in the top 3 cm of the soil column treated with alum ranged from 400 to 500 mV for the initial 7 days and then reduced gradually to 150 mV (Fig. 3.2 c), while the Eh of the soil treated with $FeCl_3$ decreased to -50 mV (Fig. 3.2 d). About 42 days were needed to reach 200 mV in the top 3 cm of the $FeCl_3$-treated soil, and then the Eh decreased in a relatively short time to -50 mV.

Floodwater pH of alum amended soil was decreased from around 7 to 4.5 after 30 days of incubation, while the pH of floodwater of the control soil remained above 6

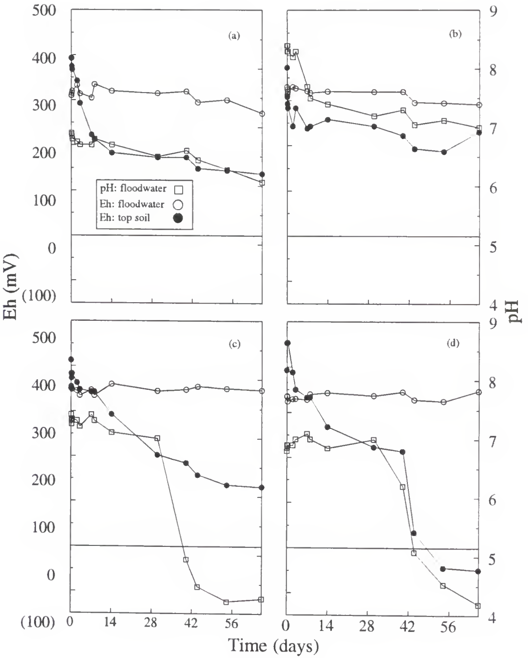

Fig. 3.2. Changes in Eh and pH of the floodwater and soil columns with time of the incubation. (a) an unamended soil, (b) $CaCO_3$ amended soil, (c) alum amended soil, and (d) $FeCl_3$ amended soil.

throughout the incubation period. The soil treated with $CaCO_3$ had an initial floodwater pH of 8.4 and the pH stayed above 7 after 7 days, while the soil amended with $FeCl_3$ had a floodwater pH of 6.5 to 7 for 28 days, which then decreased to 4.2 (Fig. 3.2 d).

Column study 1

Dissolved reactive P (DRP) flux between soil and floodwater. The changes in DRP concentrations with time in the floodwater of unamended and chemically amended soils are shown in Fig. 3.3 and Fig. 3.4. Floodwater DRP concentrations in unamended soils increased from 150 μg P L^{-1} at the beginning of flooding to 700 μg P L^{-1} at 8 weeks of incubation, and then decreased to about 550 μg P L^{-1}. Among the Ca-based amendments, $CaCO_3$ and $Ca(OH)_2$ were more effective in decreasing floodwater DRP concentrations than dolomite ($CaMg(CO_3)_2$) (Fig. 3.3 c). All rates of $CaCO_3$, except a low rate (9 g kg^{-1} soil) were shown to make no difference in P release (Fig. 3.3 a). In $Ca(OH)_2$ amended soil, the highest rate showed that DRP concentration in the floodwater was close to the baseline throughout the incubation period. The mixture of $CaCO_3/Ca(OH)_2$ was similar in DRP concentration of the floodwater to $CaCO_3$ and $Ca(OH)_2$ amended soil.

The low rates of $CaCO_3$ and $Ca(OH)_2$ treatments (90 mmols kg^{-1}) could minimize a floodwater DRP concentration up to 30% and 44% of the DRP concentration of the control (unamended soil) floodwater, respectively (Table 3.2). Higher rates of $CaCO_3$ and $Ca(OH)_2$ ($>$152 mmols kg^{-1}) could not increase the reduction of floodwater DRP effectively. However, the highest rate of $Ca(OH)_2$ treatment (1014 mmols kg^{-1}) maintained a low DRP concentration throughout the 12 weeks of incubation period (Table 3.2). Crystalline calcite precipitation probably was one of the main reasons for

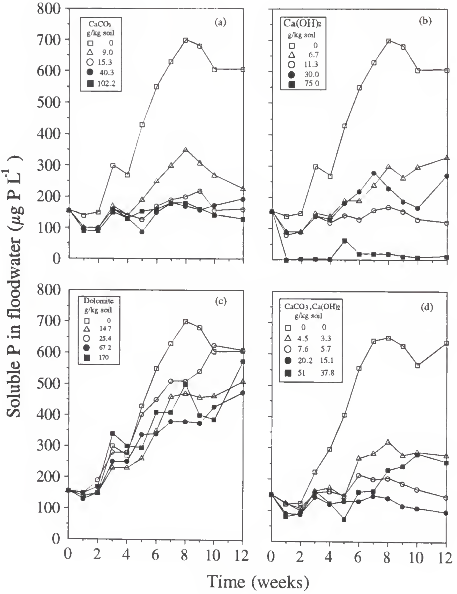

Fig. 3.3. Effect of chemically amended soils on dissolved reactive P in the floodwater with time of incubation.

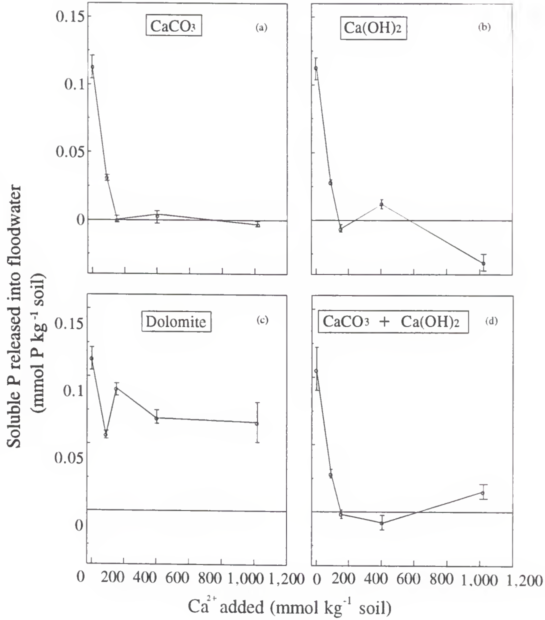

Fig. 3.4. Effects of Ca materials ($CaCO_3$, $Ca(OH)_2$, $CaMg(CO_3)_2$ and mixture of $CaCO_3$ and $Ca(OH)_2$) on immobilizing soluble P in the floodwater.

Table 3.2 Effect of soil application of calcium based amendments on soluble P released into the water column. Areal rates of application were calculated based on soil bulk density of 0.28 g cm^{-3}, and application to surface 20 cm soil. Multiply g kg^{-1} by a factor of 56 to obtain g m^{-2}.

Chemical Amendment	Rate of application		12-weeks after application Floodwater	
	g kg^{-1} soil	mmoles Ca^{2+} kg^{-1}	DRP ug L^{-1}	pH
$CaCO_3$	0	0	746	7.17
	9.0	90	226	7.62
	15.3	153	160	7.92
	40.3	403	193	7.90
	102.2	1022	129	7.84
$Ca(OH)_2$	0	0	746	7.17
	6.7	90	329	7.56
	11.3	152	121	7.92
	30.0	405	272	7.95
	75.0	1014	12	8.05
$CaMg(CO_3)_2$	0	0	746	7.17
	14.7	90	509	7.30
	25.4	151	609	7.43
	67.2	404	474	7.58
	170.0	1012	574	6.75

maintaining low DRP in the floodwater treated with $Ca(OH)_2$. This could have occurred when the calcite forming in $Ca(OH)_2$ amended soil is precipitated with phosphate, resulting in formation of amorphous Ca-P. Also, the possibility of soluble P adsorption together with organic matter on precipitating calcite has been reported (Prepas et al., 1990). Calcite is known to adsorb organic matter (White, 1975). Floodwater pH was well poised at about 7.2 in unamended soil to 8 in the highest rate of $CaCO_3$ and $Ca(OH)_2$ amended soils (Table 3.2). Figure 3.4 shows that an effective rate in P reduction in the floodwater of the soils treated with Ca-based chemicals was about 153 mmols Ca^{2+} kg^{-1}. All rates of dolomite-amended soils released 0.05 and 0.1 mmols P kg^{-1} during the entire 12 weeks of incubation (Fig. 3.4 c). Large amount of Mg in the amended soil may be responsible for increased floodwater P (Martens and Harris, 1970). The concentrations of Ca, Mg, and dissolved inorganic C were increased gradually with application of lime materials. The concentrations in the floodwater treated with $CaCO_3$ were increased sharply at low rates (< 0.2 Ca^{2+} mols kg^{-1}), followed very little or no increase in concentration (Fig. 3.5 a). The soils amended with $Ca(OH)_2$ had higher concentrations of Ca, Mg, and dissolved inorganic C than $CaCO_3$ amended soils.

Alum and $FeCl_3$ treatments also were effective in maintaining low floodwater P concentrations (Fig. 3.6). Dissolved reactive P concentration in the floodwater of an unamended soil in this batch ranged from 150 to 1000 μg L^{-1}. Generally, an increased chemical rate of all chemically amended soils reduced DRP release in the floodwater. High rates (> 14.5 g alum or 43.5 mmols Al^{3+} kg^{-1}) of alum treatments could maintain DRP concentration less than 100 μg P L^{-1} in the floodwater (Fig. 3.6 a), while even the

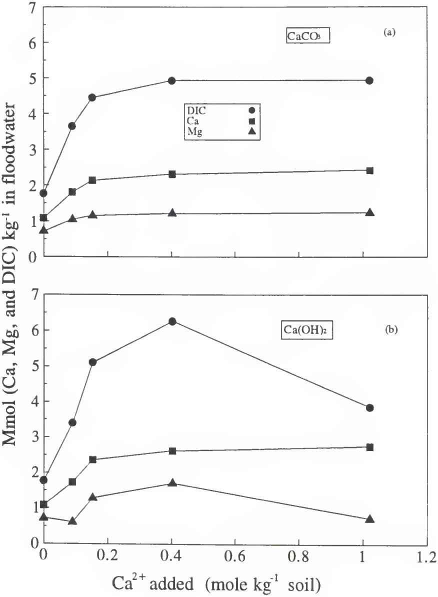

Fig. 3.5. The concentrations of Ca, Mg, and dissolved inorganic carbon (DIC) in the floodwater as influenced by lime materials.

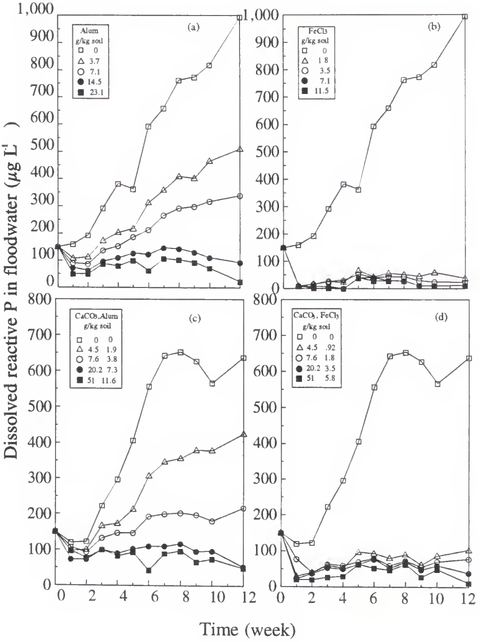

Fig. 3.6. Effects of chemically amended soils (alum, $FeCl_3$, and mixtures of $CaCO_3$ with alum or $FeCl_3$) on dissolved reactive P in the floodwater with time of the incubation.

lowest rate of $FeCl_3$ treatment reduced DRP concentration to less than about 50 μg P L^{-1} throughout 12 weeks of incubation period (Fig. 3.6 b).Also, the mixtures of $CaCO_3$ with either alum or $FeCl_3$ also showed the same pattern in DRP reduction in the floodwater as individual alum and $FeCl_3$ treatments. Higher than 7.3 g alum kg^{-1} in the mixtures of $CaCO_3$/alum could maintain dissolved P at less than about 50 μg P L^{-1} in the floodwater, while 0.92 g $FeCl_3$ kg^{-1} in the mixture of $CaCO_3$/$FeCl_3$ decreased the concentration to about 100 μg P^{-1} L^{-1} (Fig. 3.5 c, d). However, the mixures of $CaCO_3$/$FeCl_3$ were less effective in removing floodwater DRP than $FeCl_3$ alone, indicating that increased pH due to $CaCO_3$, may have inhibited the formation of iron P compounds. However, the mixture of $CaCO_3$/alum was shown to be better than alum alone amended soil in P (Fig. 3.7). The combinated treatments ($CaCO_3$/alum) were reported to be effective in controlling macrophytes and shoreline algae (Babin, et. al., 1992) and soluble P (Yuan and Lucas, 1989). In this incubation study, floodwater pH was not influenced significantly by any of the amended soils, indicating high pH buffering capacity of Lake Apopka marsh soil. Soil amended with $Ca(OH)_2$ increased floodwater pH up to 8.1, while the range of pH of floodwater treated with $CaCO_3$ was 7.3 to 7.6 (Table 3.3). The floodwater pH treated with alum was around 7, whereas $FeCl_3$ treatments at the highest rate (7.1 g kg^{-1}) decreased floodwater pH to 5.47 (Table 3.4). Alum treatments showed clearly that higher rates (>20 mmols Al^{3+} kg^{-1} soil) were required to maintain a minimum soluble P concentration, while the soil treated with $FeCl_3$ at less than 10 mmols Fe^{3+} kg^{-1} was enough to control DRP in the floodwater (Fig. 3.7). Conclusively, all $FeCl_3$ treatments had the lowest floodwater DRP concentrations, whereas alum treatments were similarly

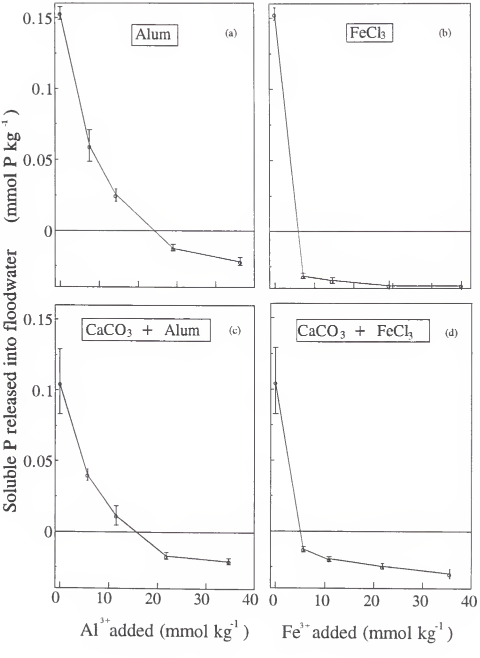

Fig. 3.7. Effects of alum, $FeCl_3$, and the mixtures of $CaCO_3$ with alum or $FeCl_3$ on immobilizing water soluble P in the floodwater.

Table 3.3 Effect of soil application of alum and ferric chloride on soluble P release into the water column. Areal rates of application were calculated by assuming soil bulk density of 0.28 g cm^{-3} and application of chemical to surface 20 cm soil. Multiply g kg^{-1} by a factor of 56 to obtain g m^{-2}.

Chemical Amendment	Rate of application		12-weeks after application Floodwater	
	g kg^{-1} soil	mmoles $(Al,Fe)^{3+}$ kg^{-1}	DRP ug L^{-1}	pH
Alum	0	0	746	7.17
	3.7	11.1	511	7.10
	7.1	21.3	293	7.28
	14.5	43.5	93	7.11
	23.1	69.3	23	7.01
$FeCl_3$	0	0	746	7.17
	1.8	11.1	37	6.83
	3.5	21.5	23	6.17
	7.1	43.7	11	6.50
	11.5	70.0	11	5.47

Table 3.4 Effect of soil application of combinations of $CaCO_3$ with other chemicals on soluble P released into the water column. Areal rates of application were calculated by assuming soil bulk density of 0.28 g cm^{-3} and application of chemical to surface 20 cm soil. Multiply g kg^{-1} by a factor of 56 to obtain g m^{-2}.

Chemical Amendment	Rate of application		12-weeks after application Floodwater	
	g kg^{-1} soil ($CaCO_3$)	g kg^{-1} soil	DRP ug L^{-1}	pH
$CaCO_3$ + $Ca(OH)_2$		$Ca(OH)_2$		
	0	0	746	7.17
	4.5	3.3	277	7.71
	7.6	5.7	144	7.83
	20.2	15	96	8.37
	51	38	255	8.33
$CaCO_3$ + alum		alum		
	0	0	746	7.17
	4.5	1.9	426	7.70
	7.6	3.8	218	7.50
	20.2	7.3	54	6.99
	51	12	50	7.06
$CaCO_3$ + $FeCl_3$		$FeCl_3$		
	0	0	746	7.17
	4.5	0.9	103	7.50
	7.6	1.8	78	6.95
	20.2	3.5	39	6.95
	51	5.8	11	6.83

effective only when applied at higher rates. Similar trends were observed in the soils treated with $CaCO_3$/alum and $CaCO_3/FeCl_3$ combinations, indicating that Al and Fe play a more significant role than $CaCO_3$ in controlling DRP concentration in the combined treatments. Calcium hydroxide treatments also were shown to be more effective in controlling soluble P and pH than soil amended with $CaCO_3$. One explanation for this is that $Ca(OH)_2$ dissociates and forms calcium carbonates easily in the high pH condition. The newly formed crystalline calcite may be small in size and provide a relatively large surface area for P adsorption. The mechanism associated with phosphate adsorption onto calcite is the molecular exchange of CO_3^{-2} and PO_4^{-3} on the surface of growing calcite crystal (Ishikawa et al., 1981).

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

$3CO_3^{-2}$ (solid) + $2PO_4^{-3}$ (liquid) $\rightarrow$ $3CO_3^{-2}$ (liquid) + $2PO_4^{-3}$ (solid)

Phosphorus distribution in amended soils. Soil P fractionation indicated minimal changes in HCl-RP (Ca-bound P) and NaOH-RP (Al- and Fe-bound P) in the soils treated with $CaCO_3$ and dolomite (Fig. 3.8 a, c). The HCl-RP fraction was increased with increasing amounts of $Ca(OH)_2$, applied either alone or in the combination with $CaCO_3$, while the NaOH-RP fraction decreased with increasing $Ca(OH)_2$ application (Fig. 3.8 b, d). Results suggested that transformation of Fe/Al-P to Ca/Mg-P at a high pH probably occurred during the incubation period. Only the highest rate of $Ca(OH)_2$ treatment could raise floodwater pH to 8.1. In the system at pH 8.5 to 9, calcium carbonate would be expected to precipitate slowly; at the same time P probably is coprecipitated on crystalline calcite (Schmid and Mckinney, 1969; Otsuki and Wetzel, 1972). Some

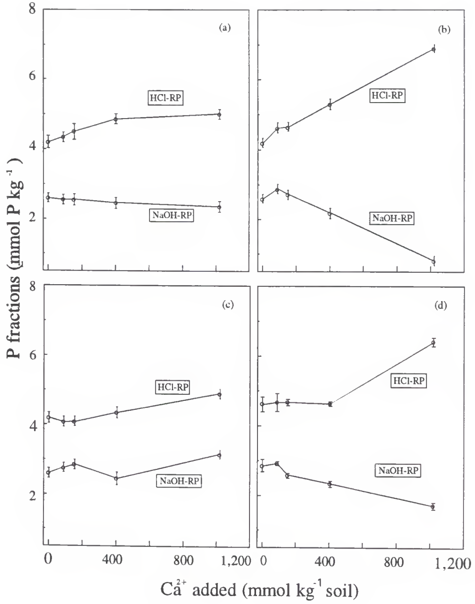

Fig. 3.8. Effects of Ca-based amendments on inorganic P (NaOH-RP and HCl-RP) of the amended soils. a) $CaCO_3$, b) $Ca(OH)_2$, c) dolomite, and d) mixture of $CaCO_3$ with $Ca(OH)_2$).

mechanisms of P inactivation by Ca reported for soils are 1)coprecipitation with calcite (Murphy et al., 1983), 2) chemi-sorption of phosphate on calcite resulting in formation of amorphous calcium phosphates (Stumm and Morgan, 1981), and 3) simple adsorption on calcite/particles (Cole et al., 1953). Hsu (1971) reported that there is no difference between chemi-sorption and precipitation.

Alum and $FeCl_3$, applied either alone or in combination with $CaCO_3$, had minimal effect on HCl-RP, while NaOH-RP fractions were increased by the high rates of $FeCl_3$ treatment (Fig. 3.9). Only a high rate of alum treatment decreased the floodwater pH to 7, whereas a high rate of $FeCl_3$ treatment lowered floodwater pH to about 5.5 (Table 3.3). The insignificant change of pH in the soil solution may be responsible for the minimal effect on inorganic P in the soil. Figures 3.8 and 3.9 showed that HCl-RP concentration was higher than NaOH-RP concentration in the soil, regardless of whether the soils were amended or not.

Solubility of P compounds in floodwater and porewater. Calculated solubility diagrams indicated that the floodwater and porewater DRP concentrations in soils amended with lime materials probably were controlled by the solid phases of Ca P compounds (Fig. 3.10). Dissolved reactive P concentrations in the floodwater of the amended and unamended soils were supersaturated with respect to apatite, but addition of higher amounts of $CaCO_3$ and $Ca(OH)_2$ resulted in equilibration or supersaturation with respect to β-tricalcium phosphate (β-TCP), and intermediate between β-tricalcium (β-TCP) and octacalcium phosphate (OCP) (Fig. 3.10 a). In the porewater of all chemically amended soils, DRP was shown to be equilibrated or supersaturated with respect to β-

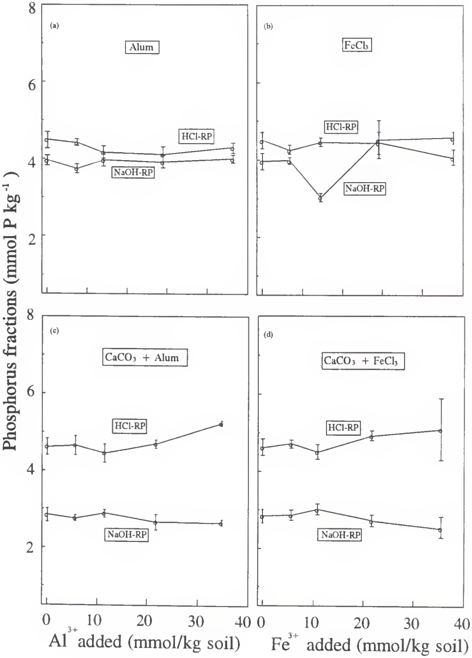

Fig. 3.9. Effects of chemically amended soils (alum, $FeCl_3$, and mixtures of $CaCO_3$ with alum or $FeCl_3$) on distribution of soil inorganic P (NaOH-RP and HCl-RP).

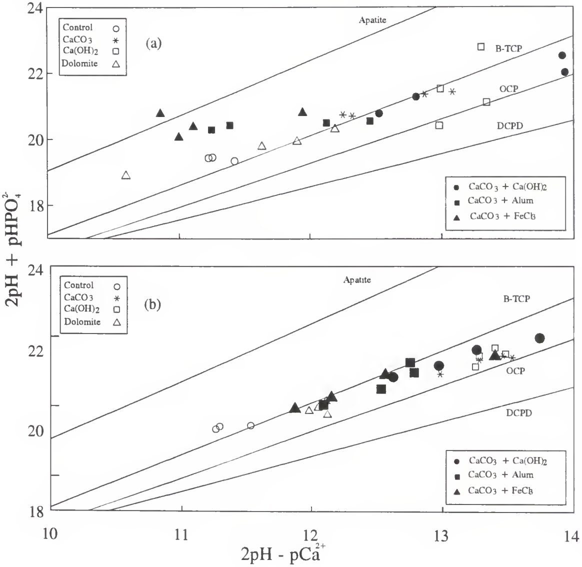

Fig. 3.10. Solubility diagrams of Ca phosphate compounds and P solubility changes in the floodwater (a) and porewater (b) treated with various chemicals. β-TCP: beta-tricalcium phosphate, OCP: octacalcium phosphate, DCP: dicalcium phosphate.

TCP (Fig.3.10 b). This could be attributed to the high potential of Ca and phosphate in the porewater. Floodwaters of the mixtures of $CaCO_3$ and alum or $FeCl_3$ also were supersaturated with respect to hydroxyapatite. However, the DRP concentration in the porewater of the soils treated with either $CaCO_3$ alone or in combinations with alum/$FeCl_3$ was in equilibrium or supersaturation with β-TCP (Fig. 3.10 b). The relationship between Ca and DRP in the floodwater (Fig. 3.11) also supports that Ca-bound P compounds probably were major compounds in controlling DRP concentrations.

A solubility diagram based on Fe-P and Al-P compounds showed that floodwater DRP concentrations in soils amended with alum/$FeCl_3$ were controlled by $FePO_4$ and $AlPO_4$ that are more soluble than variscite and strengite (Fig. 3.12). However, DRP concentrations in porewater of the soil treated with higher amount of alum and $FeCl_3$ were shown to be supersaturated with respect to variscite (Fig. 3.12 b). Ion activity products (IAP) were calculated to determine which minerals would control P concentrations in the porewater of the various chemically amended soils. Mean values of the pIAP (Table 3.5) showed that DRP in the porewaters of unamended and chemically amended soils were supersaturated with respect to hydroxyapatite. Also, β-TCP wassupersaturated with respect to soils amended with $CaCO_3$ and $Ca(OH)_2$. The calculated pIAP for Al/Fe P compounds indicated that alum treated soil was supersaturated with respect to variscite and wavellite, whereas $FeCl_3$ treated soil was supersaturated with respect to strengite and $FePO_4$. Also, to determine if carbonate minerals could be controlling P concentrations in the amended and unamended soils, the pIAP of carbonate minerals were calculated (Table 3.6). These data indicated that

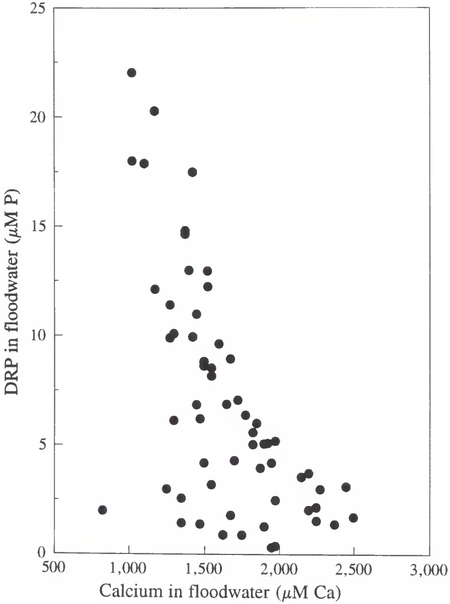

Fig. 3.11. Relationship between DRP concentration and water-soluble Ca in the floodwater of the chemically amended soils and unamended soil.

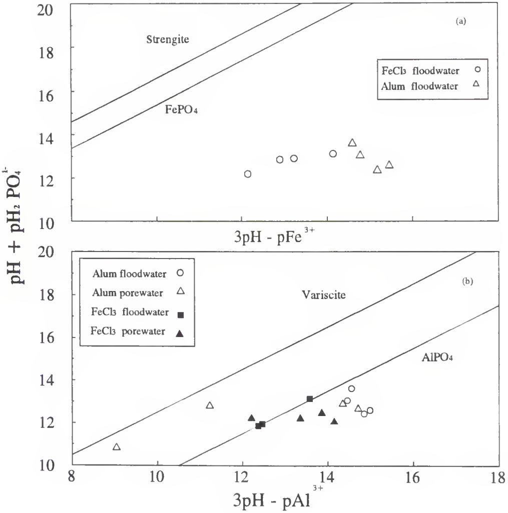

Fig. 3.12. Solubility diagrams of Al and Fe P compounds and P solubility changes in the floodwater as influenced by applying $FeCl_3$ and alum.

Table 3.5. Average pK values of selected phosphate minerals in porewater of chemically amended Lake Apopka marsh soils in Column study 1.

Phosphorus Minerals	pK	Control	Chemically amended soils				
			CaCO$_3$	Ca(OH)$_2$	Alum	FeCl$_3$	CaCO$_3$/ Alum
		pIAP ± S.D (range)					
Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$	119	106±1.3 (105-107)	99.8±0.4 (99-100)	100±1.2 (99-101)	116±2.6 (107-128)	114±7.2 (107-123)	101±4.2 (96-103)
Beta-tricalcium β-$Ca_3(PO_4)_2$	28.9	30±0.5 (29-31)	28.4±0.1 (28-28.4)	28.5±0.4 (28-29)	32.6±2.6 (30-36)	31.9±2.0 (30-35)	28.6±1.3 (27-31)
Octacalcium $Ca_4H(PO_4)_3 2.5H_2O$	46.9	50.6±0.5 (50-51)	49.1±0.1 (20-21)	49.4±0.6 (48.5-50)	53.9±3.1 (51-58)	52.7±2.4 (50-56)	49.4±1.6 (48-60)
Dicalcium P Dihydrate $CaHPO_4 2H_2O$	18.9	20.6±0.1 (20-21)	20.7±0.1 (20-21)	20.8±0.2 (20-21)	21.2±0.5 (20-22)	20.9±0.5 (21-22)	20.7±0.4 (20-22)
Variscite $AlPO_4$	22.1 19.1	22.8±1.1 22.8±1.1 (21-24)	26.3±0.3 26.3±0.3 (26-27)	26.5±0.3 26.5±0.3 (28-29)	21±1.0 21±1.0 (20-21)	20.4±0.5 20.4±0.5 (20-21)	24.2±1.3 24.2±1.3 (22-26)
Strengite $FePO_4$	26.4 25.9	25±0.6 25±0.6 (24-25.6)	31.5±0.6 31.5±0.6 (30.6-32)	32.2±1.0 32.2±1.0 (30-33)	24.1±0.9 24.1±0.9 (23-25)	23.8±0.6 23.8±0.6 (23-24)	29.8±1.4 29.8±1.4 (27-31)
Wavellite $Al_3(PO_4)_2(OH)_3 5H_2O$	73.6	78.6±3 (74-80)	86.9±0.7 (78-88)	87.3±0.5 (86-88)	74.1±2.1 (71-76)	72.3±1.2 (71-73)	81.3±3.5 (77-87)
Whitlockite $Ca_{18}(Fe,Mg)H_2(PO_4)_{14}$	222	233±3.4 (230-234)	230±0.7 (229-231)	232±3.4 (227-235)	248±14 (233-266)	242±12 (231-257)	230±7 (222-233)

Values in parenthesis indicate the range of ion activity products.

Table 3.6 Mean pK values of selected carbonate mineral in chemically amended Lake Apopka marsh soils used in Column study 1.

Chemical	Aragonite (pK=8.16)			Calcite (pK= 8.34)			Dolomite (pK=17)		
Amendments	$pIAP^M$	S.D	range	$pIAP^M$	S.D	range	$pIAP^M$	S.D	range
Control	10.3	0.7	9.6-11.1	10.3	0.7	9.6-11.1	26.8	1.4	25.3-28.2
$CaCO_3$	7.5	0.2	7.3-7.8	7.5	0.2	7.3-7.8	20.8	0.5	20.5-21.5
$Ca(OH)_2$	7.3	0.3	6.9-7.7	7.3	0.3	6.9-7.7	20.3	0.8	19.5-21.3
Alum	11.6	1.9	9.8-14.0	11.6	1.9	9.8-14	27.8	3.5	24.3-32.4
$FeCl_3$	11.2	1.4	10.1-13.2	11.3	1.4	10.1-13.2	27.4	3.2	25.3-32.1
$CaCO_3$/Alum	7.9	0.5	7.5-8.5	7.9	0.5	7.5-8.5	20.5	1.5	18.9-22.5
$CaCO_3/FeCl_3$	8.3	0.8	7.4-9.2	8.3	0.8	7.4-9.2	20.9	1.8	18.8-23.0

porewaters of the soils amended with $CaCO_3$, $Ca(OH)_2$, and mixtures of $CaCO_3$ with alum or $FeCl_3$ were supersaturated with respect to aragonite and calcite.

The unamended soil was undersaturated with respect to any amorphous Ca P compounds and carbonate minerals, and apparently was supersaturated with respect to hydroxyapatite, strengite, $FePO_4$, and possibly variscite. However, experimental observation of an IAP larger than the corresponding K_{sp} in a solution is not conclusive evidence of precipitation (Sposito, 1984), as precipitation may be kinetically inhibited. Hydroxyapatite is unlikely precipitated since its formation may be hindered by the presence of Mg (Martens and Harriss, 1970), carbonate (Ferguson, 1969; Stumm and Leckie, 1970), and organic acids (Inskeep and Silvertooth, 1988). Lindsay (1979) proposed that soluble soil $FePO_4$ and $AlPO_4$ are more likely formed in the soil systems rather than solid strengite and variscite. As described earlier, Al/Fe-bound P compounds ($FePO_4$ and $AlPO_4$) formed in unamended soil likely were more readily soluble than solid strengite and variscite for controlling soluble P. The findings from this study explain the processes that cause P release to floodwater from the soil to the floodwater. Phosphorus released from the bottom soil (>20cm depth) may be trapped by Ca in soil, and especially by Fe^{3+} in the oxidized layer of top soil. Aged and/or newly formed Ca-bound P in this slightly acidic condition may be amorphous compounds or surface P-complex developed on the solids.

Non-apatite Ca-P, such as β-TCP, OCP, amorphous Al hydroxide, and iron oxide phosphate compounds probably controlled soluble inorganic P in the floodwater and porewater of chemically amended soils. Moore et al. (1991) predicted that a more soluble mineral phase such as β-$Ca_3(PO_4)_2$ and $Ca_{18}(Mg,Fe)H_2(PO_4)_{14}$ (whitlockite), may be forming instead of apatite in Lake Apopka sediments. In Lake Okeechobee sediments that contained relatively high Al and Fe, P uptake was correlated with Al/Fe oxyhydroxide and organically bound Al (Olila and Reddy 1993).

From the results presented, it can be concluded that 1) Ca bound-P was dominant over Al/Fe-bound P in unamended soil, but Al and Fe still play an important role in controlling DRP, 2) Ca-, Al-, and Fe-bound P compounds were considered to be very soluble, 3) P coprecipitation usually coupled with the formation of crystalline calcite did not likely occurr in unamended soil because of its acidic conditions, 4) physical adsorption probably was a major mechanism in unamended soil rather than precipitation, 5) $Ca(OH)_2$ treatment gave a significant change in inorganic P distribution, indicating that Ca P precipitation and coprecipitation controlled P, while $CaCO_3$ treatment showed little effect on inorganic P transformation, and 6) $FeCl_3$ treatment increased P reduction in the floodwater and more NaOH-RP formation than did the soil amended with alum.

Mineralogical composition of the chemically amended soils. Results of X-ray diffraction analysis (XRD) indicated that smectites, kaolinite, quartz, and weddellite were identified in the silt or clay fractions of all soils (Fig. 3.13), but carbonate mineral as calcite could be found only in the $Ca(OH)_2$ amended soil (Fig. 3.14). Calcite was detected in the silt of the $Ca(OH)_2$ amended soil. Other minerals such as smectite, quartz, kaolinite, and calcium oxalate (weddellite) were identified in the unamended soil. Quartz was also identified along with calcite in the silt of $Ca(OH)_2$ amended soil. A calcium oxalate mineral, weddellite ($Ca_2C_2O_4 \bullet 4H_2O$), which probably was formed during NaOCl

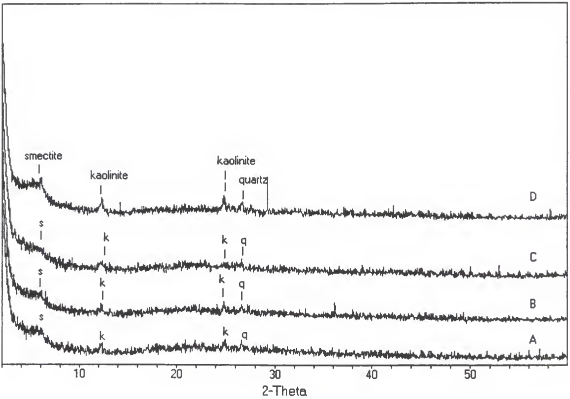

Fig. 3.13. X-ray diffraction pattern for clay of (a) unamended soil, (b) $Ca(OH)_2$ amended soil, (c) alum amended soil, and (d) $FeCl_3$ amended soil. (s is smectite, k is kaolinite, and q is quartz).

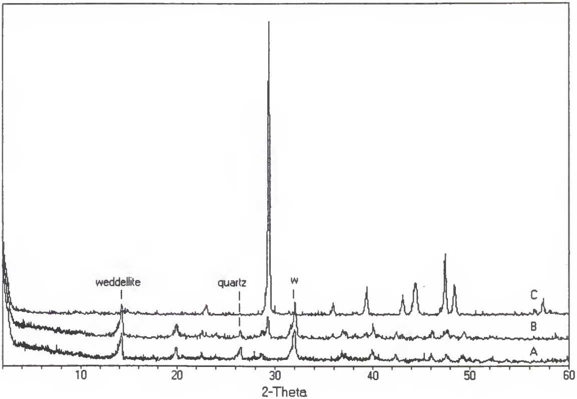

Fig. 3.14. (a) X-ray diffraction patterns of silt, unamended soils (b) silt, $Ca(OH)_2$ amended soil, and (c) a calcite standard (presented for comparison); Peak labels: w is weddellite. Most of the other peaks can be accounted for weddellite and quartz.

pretreatment, was detected in the control and all chemically amended soils. No crystalline Ca-P and Al/Fe-P minerals were identified in any of the samples. Identification of amorphous Ca-P compounds could be done by other techniques such as scanning electron microscopy and energy dispersive X-ray.

Column study 2

Soluble P flux between soil and floodwater. Floodwater DRP concentrations in unamended soil increased from 160 μg P L^{-1} at the onset of flooding to 600 μg P L^{-1} after 12 weeks of incubation (Fig. 3.15). Among the lime materials, $Ca(OH)_2$ treatment was most effective in floodwater DRP reduction, particularly during first 5 weeks; then, floodwater DRP concentration increased sharply (Fig. 3.15 a).

Ferric chloride treatments (1.8 and 7.2 g kg^{-1}) had the lowest floodwater DRP concentrations during the incubation period (Fig. 3.15 b). Alum treatments (14.5 g kg^{-1}) were similarly as effective as the treatment with 1.8 g kg^{-1} of $FeCl_3$ (Fig. 3.15 b, and Table 3.7). The results attained from alum treatments were similar in two different ways (pellet and solution). Two mixtures of $CaCO_3$ combined with $FeCl_3$ and alum looked similar in their effectiveness of DRP reduction (Fig. 3.15 a) even though the chemical rate in the $CaCO_3$/$FeCl_3$ mixture was lower than in the $CaCO_3$/alum mixture. Conclusively, all amended soils maintained DRP concentrations in the floodwater at less than the initial concentration. Figure 3.16 shows linear relationships between mass of P flux (μg P) to the floodwater from the soil column and the incubation time. A positive slope for unamended soil (control) indicated that DRP was released from the soil column, while a negative slope meant that the DRP was retained in the chemically amended soils.

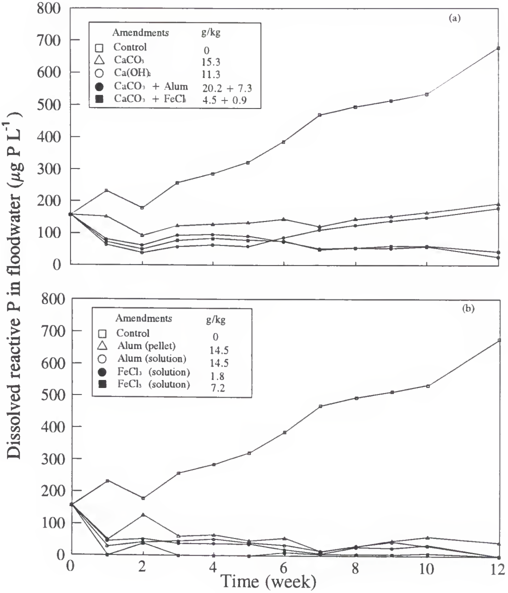

Fig. 3.15. Effects of the selected rates of chemically amended soils on DRP concentration in the floodwater when the chemicals are applied to the top 3 cm of the soil column. The rate of each chemical used in this incubation study was selected from Column study 1.

Table 3.7. Dissolved reactive phosphorus (DRP) concentration in porewater of the selected rates of chemically amended soils in Column study 2.

Treatment	Rate g kg^{-1}	DRP concentration in porewater	
		0-3 cm	3-14 cm
		(mean ± sd) (mg L^{-1})	(mean ± sd)
Control	0	0.85 ± 0.05	4.52 ± 0.42
$CaCO_3$	15.3	0.43 ± 0.34	3.71 ± 0.34
$Ca(OH)_2$	11.3	0.36 ± 0.04	4.35 ± 0.68
Alum pallet (p)	14.5	0.08 ± 0.04	1.21 ± 0.33
Alum solution (s)	14.5	0.04 ± 0.01	1.24 ± 0.92
$FeCl_3$ (s)	1.7	0.12 ± 0.01	3.12 ± 0.04
$FeCl_3$ (s)	7.1	0.02 ± 0.00	1.03 ± 0.38
$CaCO_3$ + Alum (p)	20 + 7.1	0.03 ± 0.01	1.27 ± 0.18
$CaCO_3$ + $FeCl_3$ (s)	4.5+ 0.9	0.23 ± 0.06	2.33 ± 0.38

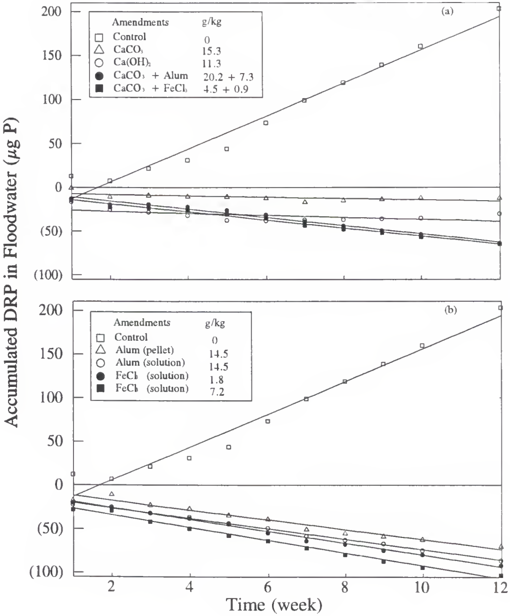

Fig. 3.16. The sum of released DRP to the floodwater until each sampling time. Positive slope (Control) indicates P released to the floodwater, while negative slopes (chemically amended soils) indicate P retained by the chemical amendments.

The effectiveness of amendments in reduction of the floodwater DRP was in the order of: $FeCl_3$ > alum > $CaCO_3$/alum or $FeCl_3$ combinations > $Ca(OH)_2$ > $CaCO_3$. Table 3.7 shows DRP concentrations of the porewater in the upper soil (top 0-3 cm) and lower soil (3-14 cm). Porewater DRP concentrations in the top 0 to 3 cm of the soils treated with $CaCO_3$ and $Ca(OH)_2$ were 0.43 and 0.36 mg L^{-1}, respectively, whereas porewater DRP concentrations with alum and $FeCl_3$ treatments were 0.04 to 0.08 and 0.02 to 0.12 mg L^{-1}, respectively. Treatments using either alum and $FeCl_3$ alone or combined with $CaCO_3$ also reduced porewater SRP concentrations significantly in the bottom soil (3 to 14 cm depth) (Table 3.7). However, a low rate of $FeCl_3$ (1.7 g kg^{-1}) application was shown to be less effective to control P in the bottom soil than in the top soil.

Table 3.8 shows comparative data in DRP reduction in the floodwater between the two application methods (Column studies 1 and 2). In comparing the effectiveness based on the values obtained from the two methods (Column studies 1 and 2), DRP was retained more by the method used in Column study 2. However, the difference of DRP reduction between two methods was not significant.

Solubility of P compounds in floodwater and porewater. Solubility diagrams indicated that the floodwater and porewater DRP concentrations in amended/unamended soils may have been controlled by the solid phases of Ca P compounds (Fig. 3.17 a, b). Floodwater and porewater of unamended soil were supersaturated with respect to hydroxide apatite. Treatments with $CaCO_3$/$Ca(OH)_2$ resulted in supersaturation with respect to β-tricalcium and octacalcium phosphate in the floodwater and porewater,

Table 3.8. Mean values of pH and dissolved reactive phosphorus (DRP) concentration in porewater after 12 weeks of flooding. Two column studies were compared by total released P from the soil column for 12 weeks of incubation.

Amendments	Rate	Column Study	DRP	Released P*	pH
	(g kg^{-1})		(μg L^{-1})	(μg)	
Control	0	Column study 1	606±24	221±19	7.15±0.04
		Column study 2	677±11	203±5.5	7.20±0.03
$CaCO_3$	15.3	Column study 1	160±50	7.3±17	7.92±0.02
		Column study 2	192±10	-6.9±7.6	7.85±0.03
$Ca(OH)_2$	11.3	Column study 1	121±21	-8.0±11	7.92±0.07
		Column study 2	179±21	-30 ±10	7.95±0.35
Alum pellet (p)	14.5	Column study 1	93±33	-28±13	7.11±1.0
		Column study 2	43±12	-69±5.1	6.94±0.13
Alum solution (s)	14.5	Column study 1	ND	ND	ND
		Column study 2	0	-86±1.2	6.86±0.04
$FeCl_3$ (s)	1.7	Column study 1	37±0.0	-76±2.0	6.83±1.0
		Column study 2	0	-91±0.9	6.73±0.02
$FeCl_3$ (s)	7.1	Column study 1	11±0.0	-91±0.3	6.17±1.0
		Column study 2	0	-103±0.6	5.39±0.2
$CaCO_3$ + Alum (p)	20.2 + 7.1	Column study 1	54±13	-42±6.0	6.99±0.17
		Column study 2	26±10	-64±3.2	7.80±0.05
$CaCO_3$ + $FeCl_3$ (s)	4.5 + 0.91	Column study 1	103±28	-47±6.4	7.50±0.05
		Column study 2	43 ±16	-64±3.9	7.83±0.03

*: Negative values in column of released P indicate DRP immobilized by chemically amended soils.

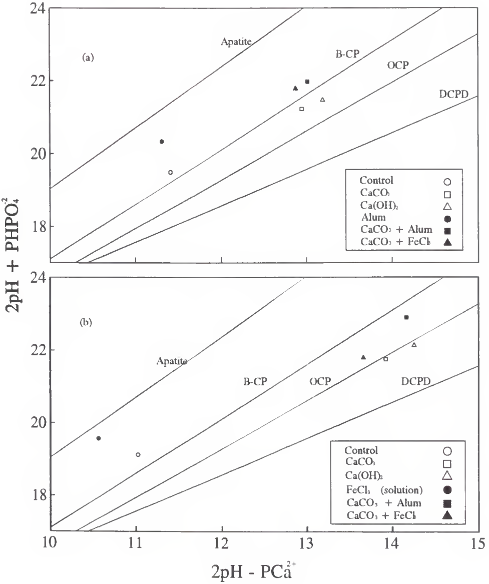

Fig. 3.17. Calculated solubility diagrams of Ca phosphate minerals and P solubility changes in (a) the floodwater and (b) the porewater treated with chemicals.

respectively. Similarly, soils amended with $CaCO_3$/alum or $CaCO_3/FeCl_3$ mixtures were supersaturated with respect to hydroxyapatite and β-tricalcium phosphate, respectively. Solubility diagrams based on Al-P compounds showed that floodwater in unamended soil and soil treated with either $CaCO_3$ alone or $CaCO_3$/alum mixtures were shown to be supersaturated with respect to variscite (Fig. 3.18 a), while porewater DRP concentrations of chemically amended and unamended soils were controlled by amorphous aluminum P ($AlPO_4$), which is more soluble than variscite. Also, calculated solubility diagrams for Fe-P compounds (Fig. 3.19 a, b) indicated that floodwater and porewater DRP concentrations were supersaturated with respect to more soluble $FePO_4$. These observations were in agreement with the results obtained from the previous experiment where amendments were uniformly mixed with the whole soil column (Column study 1).

Phosphorus distribution in soils. Inorganic P fractionation studies for the top 0-3 cm of unamended (Control) soil showed a higher NaOH-RP concentration(61 mg kg^{-1}) than HCl-RP concentration (52 mg kg^{-1}) (Table 3.9).

The bottom soil also contained more NaOH-RP than HCl-RP in both unamended and chemically amended soil (Fig. 3.20 b). The addition of calcium materials increased Ca-bound P (HCl-RP) but decreased Al/Fe-bound P (NaOH-RP). The soils amended with $Ca(OH)_2$ gave more HCl-RP than $CaCO_3$ treatments, but no change was shown in the sum of inorganic P in both treatments. This suggests that the increased fraction of HCl-RP in Ca-based amendments was probably originated from NaOH-RP. Conversely,

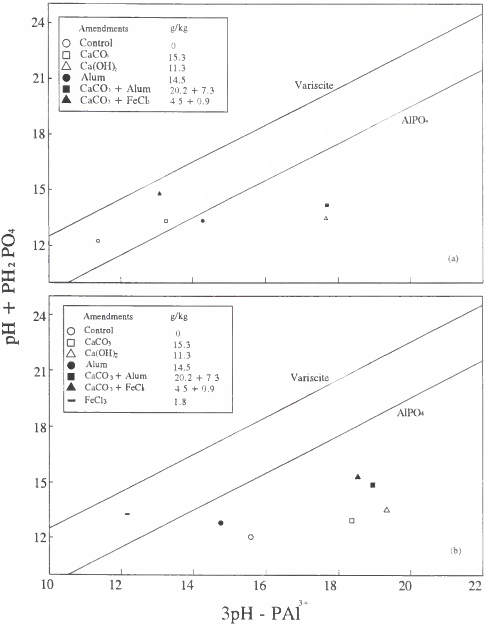

Fig. 3.18. Solubility diagrams for aluminum phosphate compounds in (a) the floodwater and (b) porewater treated with selected rates of chemical amendments. The chemically amended soils were applied to the top 3 cm of the soil column (Column study 2).

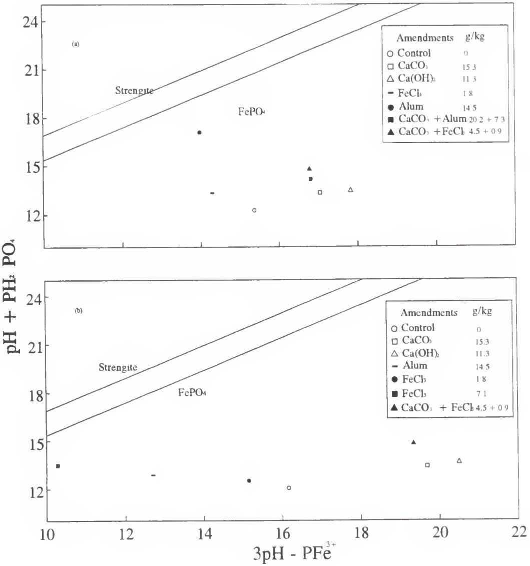

Fig. 3.19. Calculated solubility diagram of Fe phosphate minerals in (a) the floodwater and (b) porewater treated with selected rates of chemical amendments. The amendments were applied onto the top 3 cm of soil column (Column study 2).

Table 3.9. Phosphorus distribution in floodwater, porewater, and soil columns in the Column study 2. Soil P was determined by inorganic P fractionation scheme after removing porewater from sub soil by centrifugation.

Treatment	Rate	Depth in Soil Column	DRP in Floodwater	DRP in Porewater	Soil Inorganic P				Soil Organic P			Sum P
					WSP	NaOH-RP	HCl-RP	TP_i	NaOH-P_o	Residual P_o	TP_o	
	g kg^{-1}	cm	mg kg^{-1}									
Control	0	0-3	13.1±0.9	0.7±0.06	9.2±1.4	61±3.3	52±2.4	121±7	164±15	264±7.9	429±9.2	550±13
		3-14		2.0±0.34	8.6±1.7	76±7.5	45±1.9	130±10	157±11	218±14	376±14	
$CaCO_3$	15.3	0-3	-0.5±0.5	0.3±0.06	2.1±0.8	45±2.8	58±3.5	105±3	133±5.2	244±11	377±16	482±30
		3-14		1.5±0.25	7.6±2.8	61±7.5	46±1.1	114±10	146±18	236±20	382±33	
$Ca(OH)_2$	11.3	0-3	-1.7±0.6	0.24±0.03	2.5±0.6	38±7.2	63±6.5	103±3	110±16	250±6.8	359±21	464±27
		3-14		0.80±0.21	5.4±1.6	67±8.7	45±3.4	117±11	155±9.0	234±16	389±25	
Alum pallet (p)	14.5	0-3	-3.9±0.7	0.07±0.01	1.2±0.1	102±13	40±1.9	143±11	223±6.1	283±6.1	506±9.4	649±21
		3-14		1.00±0.40	4.7±0.4	70±7.0	44±2.5	118±7	144±5.2	201±19	345±16	
Alum solution (s)	14.5	0-3	-4.7±0.3	0.03±0.00	1.5±0.7	104±6.3	40±2.5	145±7	221±6.9	285±11	476±26	621±14
		3-14		0.40±0.20	3.8±0.8	68±5.7	47±0.3	118±6	143±4.0	215±7.8	366±10	
$FeCl_3$ (s)	1.7	0-3	-5.6±0.5	0.09±0.01	3.2±0.7	76±3.7	47±0.9	126±5	160±4.3	248±9.8	441±40	567±15
		3-14		0.90±0.12	8.3±2.3	69±2.7	39±0.4	117±4	162±13	242±9.3	396±13	
$FeCl_3$ (s)	7.1	0-3	-6.7±0.9	0.01±0.00	0.3±0.0	89±1.8	38±1.1	127±3	206±18	263±3.8	470±19	597±3
		3-14		0.34±0.10	3.9±0.8	68±2.4	45±3.1	117±3	136±4.9	230±2.3	366±6.4	
$CaCO_3$ + Alum (p)	20.2 + 7.1	0-33	-4.3±0.4	0.02±0.00	0.3±0.0	46±1.8	55±3.7	100±2	120±6.5	259±23	379±28	479±29
		3-14		0.55±0.08	3.2±0.5	78±4.1	46±0.6	127±4	173±25	249±6.3	423±28	
$CaCO_3$ + $FeCl_3$ (s)	4.5 + 0.91	0-3	-3.8±0.4	0.21±0.06	3.8±0.1	67±2.6	52±2.2	123±4	168±0.6	263±11	432±11	555±36
		3-14		0.70±0.30	6.3±0.6	70±10	45±5.9	122±16	68±23	239±11	408±34	

WSP: labile P, NaOH-RP: Al/Fe-bound P, HCl-RP: Ca/Mg-bound P, TP_i: sum of soil inorganic P, NaOH-P_o: Organic P, TP_o: sum of soil organic P.

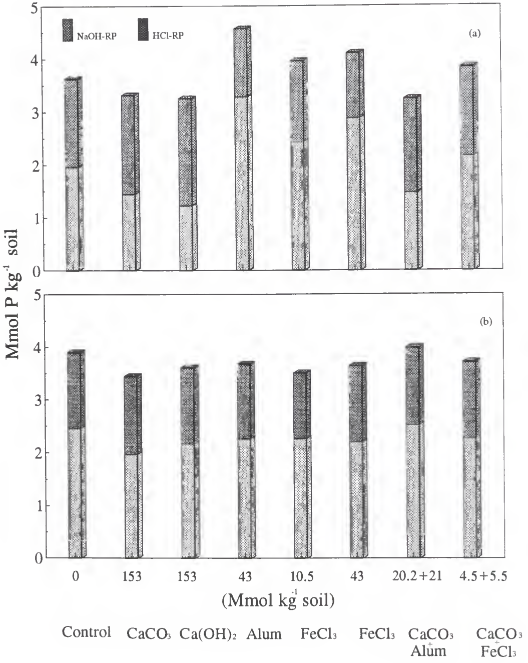

Fig. 3.20. Effects of chemically amended soils on distributing of inorganic P (NaOH-RP and HCl-RP) in the Column study 2. (a) top 3 cm depth of soil column, (b) bottom soil (3 to 14 cm depth of soil column).

alum/$FeCl_3$ treatments decreased Ca-P (HCl-RP) and increased Al/Fe-P (NaOH-RP). The soils amended with $FeCl_3$ also increased the NaOH-RP, but less than soils treated with alum. The total inorganic phosphates (TP_i) obtained from the alum amended soils was the largest among all of the chemically amended soils. Total inorganic P (TP_i) of the total P in the chemically amended soils ranged from 18 to 28%. Unamended soil had about 22% TP_i fractions, whereas alum and $FeCl_3$ treatments increased TP_i up to 28% and 25% of total soil P, respectively (Table 3.9). It may be explained that the acidic condition developed by applying alum/$FeCl_3$ into the upper soil column (top 3 cm) prompted P mineralization through the hydrolysis of organic matter and resulted in precipitation of the mineralized P with Al/Fe hydroxides and/or adsorption on the complexations of Al/Fe-organics. This is evidenced by the high concentration of 0.1 N NaOH extractable organic P (NaOH-P_o) in alum/$FeCl_3$ amended soils (Table 3.9).

Application of all chemical amendments showed minimum changes in HCl-RP and NaOH-RP concentrations in the bottom soil (3-14 cm) (Fig. 3.20 b). Water extractable P (wsp) in the unamended soil was about 8% of the TP_i, while chemically amended soils gave wsp fractions of 2, 2.4, 0.8, 2.5, 0.2, 0.3, and 3% of the TP_i for the treatments of $CaCO_3$, $Ca(OH)_2$, alum, $FeCl_3$ (1.7 g kg^{-1}), $FeCl_3$ (7.1 g kg^{-1}), $CaCO_3$/alum, and $CaCO_3$/$FeCl_3$, respectively. The DRP concentrations in the floodwater and porewater for the surface 0-3 cm soil of the unamended soil were identical (Fig. 3.21). The lime materials decreased the DRP concentration in the floodwater and porewater of the upper column soil, but the DRP concentrations in the porewater of the lower column soil seemed unaffected by the limes. Alum and $FeCl_3$ (7.1 g kg^{-1}) amendments decreased DRP

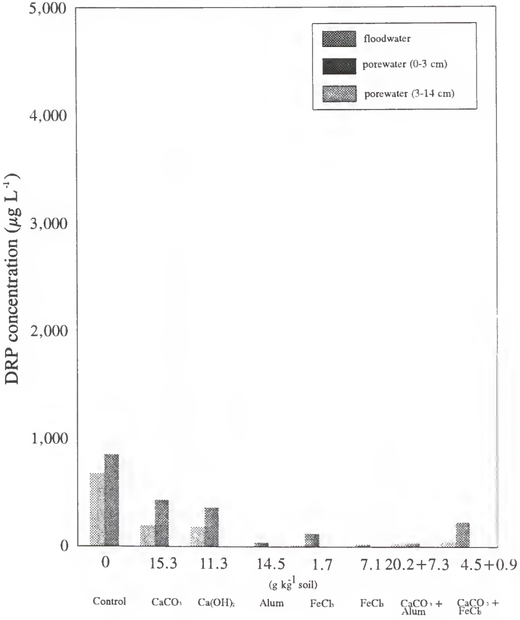

Fig. 3.21. Influence of the chemically amended soils on DRP concentrations in the floodwater, top porewater (3 cm), and bottom porewater (3 to 14 cm) in Column study 2.

concentrations in all three compartments. Not significant difference was showed in P retaining between alum application in liquid form and pellet form (Table 3.8).

Discussion

Total P content of the Lake Apopka marsh soil used in this study was 20 mmols kg^{-1} (Table 3.1). This value is in the same range, as those reported for Lake Apopka sediments (Olila, 1992). Total inorganic P accounted for 42% of total P, which is typically higher than those reported for organic soils (Hesse, 1962; Stevenson, 1982). The fractions of water-soluble P and KCl-RP were 3.5 and 4.1%, respectively. Aluminum and Fe-bound P (18 %) and Ca/Mg-bound P (19%) were evenly distributed (Table 3.10).

Throughout the incubation period, DRP reduction in $CaCO_3$ amended soil never surpassed $Ca(OH)_2$ amended soil. About 150 mmol of $Ca(CO)_3$ and $Ca(OH)_2$ kg^{-1} soil appeared to be the most effective rate that could maintain minimum DRP release (Fig. 3.4). However, the highest rate of $Ca(OH)_2$ treatment (1014 mmol kg^{-1}) could maintain DRP concentration at less than 10 $\mu g\ L^{-1}$ (Fig. 3.3 b). These results may be related very closely with the increased pH of $Ca(OH)_2$ amended soil. Only the highest rate of $Ca(OH)_2$ could raise pH above 8 in the floodwater (Table 3.2). A calcium carbonate mineral as calcite has been shown to lower P concentrations in water systems (Prepas et al., 1990). For example, adsorption of P onto $CaCO_3$ (Cole et al., 1953; Griffin and Jurinack, 1973) and/or coprecipitation with $CaCO_3$ (Otsuki and Wetzel, 1972; Freeman and Rowell, 1981) has been known for P inactivation mechanisms in calcareous sediments/soils. Adsorption of P by $CaCO_3$ is attributed to an exchange of orthophosphate with water

Table 3.10. Forms of inorganic P in chemically amended Lake Apopka marsh soils. (Column study 1)

Treatment	Rate	1 M KCl -RP	0.1 M NaOH-RP	0.5 M HCl-RP	Residual P	Total P	% of Recovery
	$g\ kg^{-1}$			$mmol\ kg^{-1}$			%
Control	0	0.72 (4.1)	3.18 (18)	3.34 (19)	8.47 (48)	17.6	89
$CaCO_3$	15.3	0.48 (2.7)	3.73 (21)	3.88 (22)	8.98 (50)	17.9	95
Alum	14.5	0.37 (2.1)	4.87 (28)	4.24 (23)	8.03 (45)	17.9	98
$FeCl_3$	1.8	0.71 (4.0)	6.20 (35)	4.31 (24)	7.10 (40)	17.9	103

Values in parenthesis are % of total P. 1M KCl-RP: loosely bound and exchangeable P, 0.1 M NaOH-RP: Al/Fe-bound P, 0.5 M HCl-RP: Ca/Mg-bound P.

molecules, hydroxide ions, and bicarbonate ions (Kuo and Lotse, 1972). The crystal surface (Stumm and Morgan, 1981; Griffin and Jurinak, 1974) and crystallization velocity of the calcite (Kleiner, 1988) were known to be primary factors, regulating P coprecipitation. The $CaCO_3$ particle has been utilized as a seed crystal, and subsequent formation of solid phases of Ca-P such as octacalcium and dicalcium phosphate have been reported (House and Donaldson, 1986). The formation of hydroxyapatite, known as the most stable compound thermodynamically, has been reported in the laboratory experiment, which was conducted in the presence of amorphous calcium compounds as seed crystals. The amorphous Ca P compounds were believed to be precipitated as precursors for the formation of hydroxyapatite (Nancolas and Tomazic, 1974; Boskey and Posner, 1976).

The soils amended with $Ca(OH)_2$ increased Ca, Mg, and dissolved inorganic C concentrations in floodwater compared to soils treated with $CaCO_3$ (Fig. 3.5 b). The results indicate that increased Ca and pH may have caused formation of carbonate particles and/or calcium carbonate minerals that, in turn, induced P sorption. Coprecipitation of P with carbonate has been explained as one of the mechanisms for lowering P concentrations in a marl lake (Otsuki and Wetzel, 1972). Coprecipitation can occur either by simple adsorption (Cole et al., 1953 ; Griffin and Jurinak, 1981) of one compound by another, with the microcomponent adhering to the surface of the host, or by incorporation into particulate carbonate with the rapid growth of the crystals (Otsuki and Wetzel, 1972; Kleiner, 1988). Result obtained from X-ray diffraction analysis indicated that calcite was precipitated in silt and sand of the $Ca(OH)_2$ amended soil (Fig.

3.14).

Apparently, other Ca phosphate compounds also were expected to precipitate in a pH range of 6 to 8.5. Decreased DRP concentrations in the floodwaters of all $CaCO_3$ and $Ca(OH)_2$ amended soils except with the highest rate of $Ca(OH)_2$ treatment were attributed to the precipitation of amorphous Ca P compounds rather than coprecipitation of P with calcite. Thermodynamic calculations showed that the precipitation of calcium carbonate (calcite) competes with Ca phosphate (hydroxyapatite) precipitation between pH 9 and 10.5, but that hydroxyapatite precipitation by itself is responsible for the predicted low P residuals between pH 7.5 to 8.5 and above 10.5 (Ferguson et al., 1970). Also, calculated solubility diagrams indicated that the floodwater of unamended soil and chemically amended soils at low application rate were at supersaturation with respect to apatite; as rates of $CaCO_3$ and $Ca(OH)_2$ increased, saturation points moved toward to β-tricalcium phosphate (β-tcp) and octacalcium phosphate (ocp) (Figs. 3.10 and 3.17). This was attributed to high Ca potential and increased pH. Although the solubility diagrams showed supersaturation with respect to hydroxyapatite, DRP concentrations in floodwater were probably controlled by more soluble amorphous Ca-P compounds. This observation suggests that precipitation of solid phases, especially hydroxyapatite, was probably inhibited by Mg, carbonate ions, and dissolved organic acids (Stumm and Morgan, 1981; Inskeep and Silvertooth, 1988), which were high in the Lake Apopka marsh soil (D'Angello and Reddy, 1994). and low pH. Organic ligands inhibit hydroxyapatite precipitation by competing for adsorption sites on the seed crystal, thereby preventing more crystal growth (Inskeep and Silvertooth, 1988). In the natural environment, amorphous P compounds such as dicalcium P (DCP and DCPD) and octacalcium P (OCP) may dominate P compounds and serve as intermediates for the formation of apatite (Berkheiser et al., 1980). The presence of Mg appears to cause the formation of more soluble amorphous Ca-bound P compounds and a magnesian calcium carbonate rather than formation of crystalline Ca-bound P compounds and calcite/dolomite (Jenkins et al., 1971; Stumm and Morgan, 1981). Increased carbonate concentrations may also cause slower Ca phosphate crystal growth rates by substitution of orthophosphate ions with the carbonate ions in the solid form of Ca phosphate compounds (Jenkins et al., 1971). However, most of orthophosphate ions are expected to precipitate with calcium ions before calcium ions are consumed for the formation of calcium carbonate minerals in the solution containing the low carbonate concentration. The P precipitation with calcium ions is kinetically much faster than calcium carbonate precipitation (Lawrence et al., 1969).

Both Al and Fe salts have long been considered as coagulants for precipitation of P from solution. However, the effectiveness and optimum acidity for P removal have been reported very differently. For example,the optimum pH for P removal has been reported to be from 5.6 to 7.7 (Hsu, 1975). Values of pH for the least soluble aluminum P obtained from even the calculation of solubility diagrams were 4 (Cole and Jackson, 1951), 5.3 (Hsu and Jackson, 1960), 5.4 (Snoeyink and Jenkins, 1980), and 6.3 (Stumm, 1964). The results obtained from this study indicated that DRP concentrations in the floodwater of alum treatments were decreased gradually as the rate of alum increased. The highest rate of alum treatment (43.5 mmol Al^{3+} kg^{-1}) could maintain the DRP in the floodwater at less than about 80 $\mu g\ L^{-1}$ (Fig. 3.6 a). However, with even the lowest rate of $FeCl_3$ treatments, the DRP concentrations were kept lower than 50 μg^{-1} throughout the incubation period (Fig. 3.6 b). Thus, the $FeCl_3$ amended soil showed more effectiveness in DRP reduction than did alum-treated soil. Enough OH^- probably was needed to release H^+ from HPO_4^{-2} to provide PO_4^{-3} for the formation of $AlPO_4$. However, that OH^- also enhances the competition of OH^- with PO_4^{-3} for Al^{3+} (Hsu, 1976).

Conclusions

Floodwater DRP concentration in unamended soil increased up to about 1.0 from 0.15 mg L^{-1} during the incubation period, indicating that accumulated P in this soil is highly water soluble. All amendments except dolomite potentially were effective in decreasing the floodwater DRP concentrations in Lake Apopka marsh soil. Calcium carbonate, $Ca(OH)_2$, alum, and $FeCl_3$ mixed with the soil were effective in controlling labile P in the floodwater and porewater. In general, the greater amounts of amendment resulted in less DRP in the floodwater. The effective amount required for each chemical amendment to minimize P release from soil to the overlying water were 7 to 15 g kg^{-1} soil for $CaCO_3$ and $Ca(OH)_2$, 12 g kg^{-1} soil for alum, and 1-2 g kg^{-1} soil for $FeCl_3$. Based on P flux calculations and the floodwater P concentrations throughout the incubation period of both studies, the order of effectiveness of amendments were as follows; $FeCl_3 >$ alum $\geq Ca(OH)_2 > Ca(CO)_3 >$ dolomite.

Phosphorous solubility and inorganic P fractionation studies indicated that Ca-P compounds controlled P solubility in the floodwater and porewater of unamended soil.

Floodwater and porewater of soils amended with lime materials were supersaturated with respect to beta-calcium to octa-calcium phosphate compounds. Although the solubility diagrams showed that floodwater DRP in unamended soils was supersaturated with respect to hydroxyapatite, more soluble Ca-bound P was expected because of the high amounts of Mg and organic matter. Solubility diagrams indicated that Al/Fe-bound P compounds formed in chemically amended and unamended soil solutions seemed to be more soluble $AlPO_4$ and $FePO_4$ rather than variscite and strengite. The solubility calculations showed that the floodwater of unamended soil apparently was saturated with respect to variscite. Analysis of X-ray diffraction showed calcite formation in the $Ca(OH)_2$ amended soil, suggesting that P coprecipitation with calcite was the main mechanism in controlling P. No other P minerals were found in the X-ray diffraction analysis. These results indicate that amorphous Ca-, Al-, and Fe-bound P compounds were controlling DRP concentration in the soils. As an another possible reason, P levels were probably too low to be detected for XRD analysis. Although chemically amended soils affected DRP solubility in the porewater and floodwater, the inorganic P fractionation study showed that chemical treatments did not increase total inorganic P in the soil. Among the treatments in both column studies, $Ca(OH)_2$ and $FeCl_3$ appeared to be promising amendments for P inactivation in the soils. Ferric chloride treatments may provide a relatively fast control of DRP in the soil. Particularly, in Column study 2, $FeCl_3$ treatment may be recommended because of possible P precipitations as Fe^{3+} P compounds in the oxygenated layer between the water and soil columns. Low amounts of $FeCl_3$ treatment also may be recommended rather than high amounts of $FeCl_3$ for

Column study 2 because of a high hydrolyzing power and an strong affinity for P. However, ferric chloride treatment should be considered carefully because of sensitivity to redox potential change. For the purpose of long-term treatment, it is probably necessary to raise soil pH in the Apopka Lake marsh to induce the formation of more stable Ca-P compounds.

CHAPTER 4
PHOSPHATE ADSORPTION/DESORPTION CHARACTERISTICS OF CHEMICALLY AMENDED WETLAND SOILS

Introduction

The capacity of soils to retain or release P depends on physical, chemical, and biological processes functioning in overlying water and underlying soil (Gale et al. 1994). Plant and microbial uptake have been shown to be highly efficient in removing dissolved P from the water column of wetlands (Walbridge et al. 1993). Microbial P requirements are readily met under higher P loadings. Upon death of these organisms, rapid release of P increases the labile P pool of soil (Richardson et al. 1988). Removing dissolved P by plant uptake is also limited to the net annual rate of P accumulation in plant biomass (Mitch et al. 1979). Thus, P uptaken by plants will enter the litter compartment within a relatively short period of time. Kadlec (1989) states that litter and sediments are the key compartments for a wetland system in the regulation of P cycling.

Thus, biological mechanisms probably play a limited role in P retention in most wetland soils. High P-retention capacity of calcareous soils has been attributed to adsorption of P onto $CaCO_3$ (Grinffin and Jurinak, 1973) and coprecipitation with $CaCO_3$ (Otsuki and Wetzel, 1972). For non-calcareous soils, however, P sorption has been associated with Al and Fe oxides and hydroxides (Ku et al., 1978; McCallister and Logan, 1978; Sah and Mikkelsen, 1989).

Conversion of previously fertilized agricultural lands has resulted in solubilization of inorganic P and its release into the overlying water column. Porewater of these soils has a very high dissolved P concentration due to the high solubility of accumulated fertilizers used for agricultural purposes. Thus, application of chemical amendments to these soils has been suggested. In a previous study (Chapter 3), several inorganic amendments were evaluated for their effectiveness to decrease soil porewater P concentration. Although this study indicated effectiveness of amendments, it does not provide any information on P sorption characteristics of chemically amended soils. Information on sorption parameters is needed to determine the P binding strength and P retention capacity of these soils.

The objectives of this study were to 1) determine the P sorption capacities of chemically amended marsh soils, and 2) predict the P minerals controlling inorganic P concentrations in a wetland soil treated with chemical amendments.

Materials and Methods

Soil sampling. Soils used in this study were obtained from the previous study (Column Study 1, Chapter 3). In that study, Lake Apopka marsh soils were amended with various chemicals to immobilize labile inorganic P. Soils were incubated under flooded conditions for a period of 12-weeks. At the end of incubation, soils were collected, air-dried, and stored at 4°C until used in this experiment. Soils from the following treatments were used in the study.

(1) $CaCO_3$ (15.3 and 102 g kg^{-1} of soil)

(2) $Ca(OH)_2$ (11.3 and 75 g kg^{-1} of soil)

(3) $CaMg(CO_3)_2$ (25.4 and 170 g kg^{-1} of soil)

(4) $Al_2(SO_4)_3 \, nH_2O$ (14.5 and 23.5 g kg^{-1} of soil)

(5) $FeCl_3$ (1.8 and 11.5 g kg^{-1} of soil)

(6) $CaCO_3 + FeCl_3$ (51 + 5.8 g kg^{-1} of soil)

(7) $CaCO_3$ + $Al_2(SO_4)_3\ nH_2O$ (51 + 11.8 g kg^{-1} of soil)

(8) Control-1 (unflooded and air-dried soil)

(9) Control-2 (flooded for 12 weeks, then air dried)

Rates for treatments (6) and (7) were based on equal proportions of respective chemicals (1:1 weight ratio) added at 50% of their individual rates. In the earlier study (Chapter 3) it was established that the following rates were effective in immobilizing P: $CaCO_3$ (15.3 g kg^{-1}), $Ca(OH)_2$ (11.3 g kg^{-1}), alum (14.5 g kg^{-1}), and $FeCl_3$ (1.8 g kg^{-1}).

Sample characterization. Soil pH (1:1) was measured with a pH meter equipped with an electrode. Total P was analyzed using the ignition method (Saunders and Williams, 1955). Unamended and amended soils were analyzed for 0.5 M $CuCl_2 \bullet 2H_2O$-extractable Al (Juo and Kamprath, 1979); ammonium oxalate-extractable Fe and Al (McKeague and Day, 1966); citrate-dithionate-bicarbonate (CDB)-extractable Al, Fe, Ca, and Mg; and 1 M KCl-extractable Ca and Mg. The metals were analyzed using atomic absorption spectrophotometry (Perkin Elmer Model 2380).

Phosphorus adsorption experiment. A known amount of soil was placed in 50 ml centrifuge tubes and treated with standard P (KH_2PO_4) solutions of (0.06, 0.1, 0.2, 0.4, 0.6, 1, 2, 4, 6, 10, 20, 40, 60, 100 mg L^{-1}), suspended in 0.01 M KCl solution. The soil:solution ratio (w/v) was 1:100 based on the precalculated dry weight of the amended soils. The P-treated samples were allowed to equilibrate for 24 hours on an end-to-end shaker, after which they were centrifuged at 5000 rpm for 15 min. The supernatant liquid was filtered through a 0.45 μm membrane filter. The electrical conductivity (EC) and pH were measured. The remaining filtrate was acidified with one drop of concentrated H_2SO_4

(Baker Ultrapure) and refrigerated at $4^{o}C$ until analyzed for P on a Technicon AA II analyzer ascorbic method (Murphy and Riley, 1962)

Phosphorus desorption experiment. After removing the supernatant, the soil residue was suspended in 20ml of 0.01 KCl solution and shaken for 24 hours. The suspension was centrifuged and filtered as previously described. Phosphorus in the filtrate was analyzed as described above.

Calculation. The phosphorus lost from solution after the 24-hour equilibration was considered as retained by the solid phases. Hence, P adsorbed by the soil was calculated as follows: $S_1 = (C_oV - C_{24}V) / M$

where

C_o = concentration of P added, mg L^{-1},
V = volume of liquid, ml,
C_{24} = concentration of P in solution after 24-hour of equilibration period, mg L^{-1},
M = mass of dry soils, kg, and
S = P adsorbed, mg kg^{-1}.

These calculations do not take into account the amount of native P in the adsorbed phase. The total amount of P sorbed by the soil was calculated as follows:

$$S = S_1 + S_o$$

where

S_1 = amount of added P sorbed (mg kg^{-1}) and
S_o = native soil P present in adsorbed phase, (mg kg^{-1}).

The native sorbed P (S_o) was estimated using the least-squares fit of S_1 against C_{24}, which at low P concentrations followed the linear equation: $S_1 = S_o + bC_{24}$. The value of S_o (y-intercept) was considered as the native soil P present in the adsorbed phase. Adsorption parameters were obtained by fitting the data to the following adsorption isotherm equations.

(1) Linear adsorption isotherm: $S = K_dC_{24}$

where K_d (distribution coefficient in L kg^{-1}) is a constant for the retention of solute by the soil matrix, which is determined as the slope where the y-intercept is zero. The linear isotherm model has been used to describe not only reactive contaminant transport (Burkholder, 1976; Van De Pol, 1977) but also the sorption of nonreactive solutes such as the herbicide 2, 4-D (2,4-dichlorophenoxy-acetic acid), Pb, Cd, Zn, and P by the soil matrix (Travis and Etner, 1981).

(2) Freundlich isotherm: $S = K_f C_{24}^N$

where K_f is the adsorption constant in L kg^{-1} (also called the partition coefficient) and N is a constant. The S and C_{24} are as defined in the linear isotherm model. The Freundlich isotherm is defined by a nonlinear relationship. Hemwall (1957) suggested that the Freundlich isotherm also can be used to characterize precipitation. Fitter and Sutton (1975) reported that P sorption data for soils were fitted to the Freundlich adsorption isotherm. One limitation of the Freundlich isotherm is that, like the linear isotherm model, it does not imply a maximum quantity of adsorption (Travis and Etnier, 1981).

(3) Langmuir isotherm: $S = K_LS_{max}C_{24} / (1 + S_{max}C_{24})$

where K_L is a measure of the bond strength holding the sorbed solute (P) on the soil surface, S_{max} is the maximum amount of sorbed P in mmol P kg^{-1}, and S and C_{24} are as previously defined. The soil affinity for P is proportional to K_L values. In a linearized form, the Langmuir equation is written as $C_{24}/S = 1 / (K_L \times S_{max}) + C_{24}/S_{max}$.

This isotherm assumed that the surface of a solid possesses a finite number of adsorption sites. The maximum amount of P sorption occurs when the surface of a solid is covered with a closely packed adsorbed layer of P.

Results

Physico-Chemical Characteristics of Amended Soils

The chemically amended soils showed differences in pH, water-soluble P concentration, and other chemical characteristics compared to the untreated soil (Table 4.1a, b). Water-soluble P in Control-2 (0.32 mmol kg^{-1}) and dolomite-amended soils (0.24 mmol kg^{-1}) was higher than for all other treatments. The $CaCO_3$ and $Ca(OH)_2$ amended soils immobilized water-soluble P by one-half that of the Control-2, whereas alum and $FeCl_3$ amended soils had immobilized 80 to 90% of the water-soluble P (Table 4.1a). Applications at higher rates showed greater P immobilization (Table 4.1b). Soil pH was increased by 0.8 units in the $CaCO_3$ and $Ca(OH)_2$ treatments, whereas alum and $FeCl_3$ treatments soils lowered soil pH by 0.4 and 0.2 units, respectively. In comparison with control-1 and control-2, all parameters were identical, except for the water content and water-soluble P. control-2 soil had lower water-soluble P than control-1 soil.

Phosphorus Adsorption-Desorption Characteristics

Equilibrium phosphorus concentration. Equilibrium P concentration is defined as the P concentration at which the rates of adsorption and desorption are equal (Green et al., 1978). The EPC_o concept was used in predicting P movement at the sediment-water interface (McCallister and Logan, 1978).

Control-2 soil showed an EPC_o value of only 18 μM P, whereas control-1 had an

Table 4.1. Some physico-chemical properties of chemically amended soils used for the sorption test. All soil samples were air-dried after 12 weeks of the Column study 1, except for Control-1, which was the soil before flooding.

(a)

Soil Properties			Controls		Chemically amended soils				
			1	2	$CaCO_3$	$Ca(OH)_2$	$CaMg(CO_3\ )$	Alum	$FeCl_3$
pH			5.8	5.9	6.7	6.7	6.6	5.5	5.7
Water content		$g\ kg^{-1}$	490	267	150	244	307	268	225
Volatile solid		$g\ kg^{-1}$	852	849	854	849	839	852	866
Total	P	$mmol\ kg^{-1}$	20	18	16.5	16.4	17	18.7	18
	Ca		970	977	1093(77)	1082(69)	1052(51)	916	945
	Mg		159	183	178	190	336	179	182
	Al		106	101	99	99	64	138(86)	99
	Fe		100	93	86	88	87	79	99(54)
Water-Soluble	P	$mmol\ kg^{-1}$	0.71	0.32	0.15	0.16	0.24	0.06	0.09
	Ca		8.8	7.5	15	14	9	39	13
	Mg		3.2	3.6	6	6	6	22	7

(b)

Soil Properties	Chemically amended soils						
	$CaCO_3$	$Ca(OH)_2$	CaMg-$(CO_3)_2$	Alum	$FeCl_3$	$CaCO_3$ / Alum	$CaCO_3$ / $FeCl_3$
pH	7.5	8.0	6.9	5.3	5.5	7.2	7.1
Water content ($g\ kg^{-1}$)	169	248	219	209	271	216	268
Volatile solid ($g\ kg^{-1}$)	779	772	752	848	854	805	810
Total							
P ($mmol\ kg^{-1}$)	16	16.4	17.2	19.5	19.1	17.8	17.4
Ca	1896(90)	1846(86)	1686(70)	942	992	1411(95)	1407(94)
Mg	168	190	1143	178	183	187	193
Al	96	96	84	166(95)	96	128 (79)	92
Fe	84	88	75	73	119(38)	82	106 (39)
Water soluble							
P ($mmol\ kg^{-1}$)	0.12	0.09	0.23	0.05	0.04	0.05	0.05
Ca	45	53	17	73	32	79	52
Mg	15	14	13	38	19	26	20

Parenthesis indicates percent recovery (%) = 100 x (total metal of the amended soil after flooding / total metal of amended soil before flooding)

(a): Rates of selected chemically amended soils were 15.2 $g\ kg^{-1}$ for $CaCO_3$, 11.3 $g\ kg^{-1}$ for $Ca(OH)_2$, 25.4 $g\ kg^{-1}$ for $CaMg(CO_3)_2$, 14.5 $g\ kg^{-1}$ for alum, and 1.8 kg^{-1} for $FeCl_3$.

(b): Rates of selected chemically amended soils were 102 $g\ kg^{-1}$ for $CaCO_3$, 75 $g\ kg^{-1}$ for $Ca(OH)_2$, 170 $g\ kg^{-1}$ for $CaMg(CO_3)_2$, 23.1 $g\ kg^{-1}$ for alum, 11.5 $g\ kg^{-1}$ for $FeCl_3$, 51 + 11 $g\ kg^{-1}$ for $CaCO_3$ + alum, and 51 + 5.5 $g\ kg^{-1}$ for $CaCO_3$ + $FeCl_3$.

EPC_0 value of 766 μM P (Fig. 4.1). The EPC_0 for all chemically amended soils ranged from 3 to 6 μM P (Figs. 4.2, 4.3), except for soils with a lower rate of $FeCl_3$ addition, which showed a relatively high EPC_0 (9.6 μM P) (Fig. 4.3). The soils receiving higher rates of chemical amendment showed slightly lower EPC_0 than the lower rates (Table 4.2). Among the chemically amended soils, the high EPC_0 values corresponded with high concentrations of water and KCl extractable P (Table 4.2).

Sorption models. Phosphorus sorption by the two unamended soils was best described by the simple linear isotherm (Fig. 4.4). Coefficients of determination (r^2) for the control soils were > 0.90. The r^2 values of the simple linear isotherms for chemically amended soils ranged from 0.70 to 0.94, except for the 1.8 g kg^{-1} of $FeCl_3$ treatment, which was 0.44 (r^2) (Table 4.3). The soil before flooding showed minimal P sorption at solution P concentration < 600 μM P. The soil after a 12 week of incubation showed that P sorption was minimal until 150 μM P and then increased rapidly.

Phosphorus sorption isotherms in soils amended with lime materials ($CaCO_3$ and $Ca(OH)_2$) gave a good fit for the Langmuir equation ($r^2 > 0.91$), whereas soils amended with $FeCl_3$ and alum were well described by the Freundlich equation ($r^2 > 0.93$) (Table 4.3). Phosphorus sorption isotherms of soils receiving mixtures of amendments were best fit to the Freundlich equation ($r^2 > 0.93$). The Freundlich equation gave r^2 values higher than 0.92 for all soils except Control-1 soil (Table 4.3).

All chemically amended soils improved P sorption capacity at low P concentrations as compared to control-2 soil. However, a significant increase in P sorption was observed only at solution concentrations higher than 100 μM P. Soils amended with higher rates of

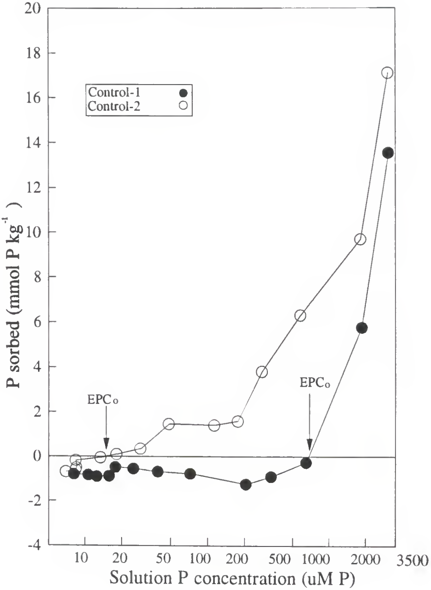

Fig. 4.1. Phosphorus sorption isotherm for Lake Apopka marsh soils showing the equilibrium P concentration (EPC_0). Control-1: the soil before flooding. Control-2: the soil after 12 weeks of incubation.

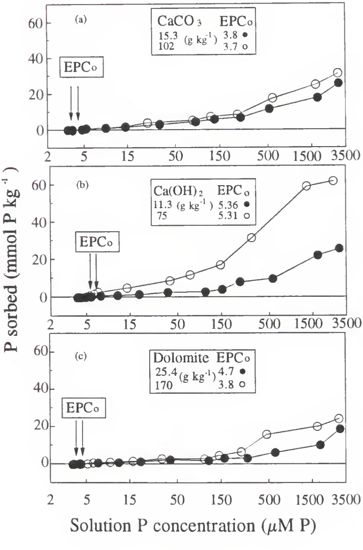

Fig. 4.2. Phosphorus sorption isotherms for the soils amended with Ca materials showing equilibrium P concentration (EPC_o). All soils were air-dried after 12 weeks of incubation.

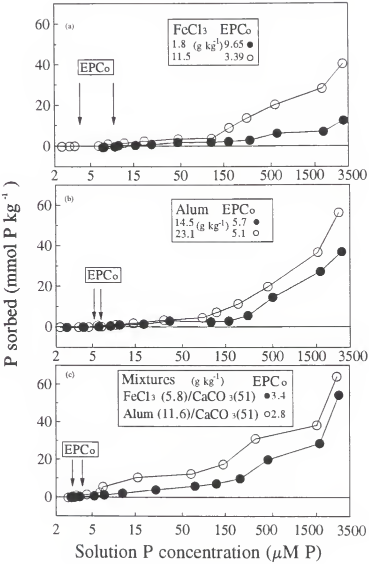

Fig. 4.3. Phosphorus sorption isotherms for the soils amended with $FeCl_3$, alum, and mixtures ($CaCO_3$/alum and $CaCO_3$/$FeCl_3$) showing equilibrium P concentration (EPC_o). All soils were air-dried after 12 weeks of incubation.

Table 4.2. Water extractable phosphorus, KCl extractable phosphorus, and equilibrium phosphorus concentration (EPC_o) of unamended (Controls) and selected chemically amended Lake Apopka marsh soils used in this sorption study.

Amended soils	Amendment Rate	Water Extractable P	0.01 M KCl Extractable P	EPC_o
	(g kg^{-1})	(mg P kg^{-1})	(mg P kg^{-1})	(μM P)
Control-1	0	23.3	25.8	766
Control-2	0	9.9	20.4	18
$CaCO_3$	15.3	4.7	11.4	3.8
	102	3.7	11.3	3.7
$Ca(OH)_2$	11.3	5.0	12.0	5.4
	75	2.8	12.2	5.3
$CaMg(CO_3)_2$	24	7.4	11.5	4.7
	175	7.1	9.9	3.8
$FeCl_3$	1.8	2.8	21.2	9.6
	11.8	1.2	7.2	4.1
Alum	14.5	1.9	8.1	5.7
	23.1	1.6	6.8	5.1
$CaCO_3$ + $FeCl_3$	51 + 5.5	1.6	9.4	3.4
$CaCO_3$ + Alum	51 + 11.5	1.6	8.2	2.8

Control-1: Lake Apopka marsh soil before flooding.
Control-2: Lake Apopka marsh soil after 12 weeks of flooding.

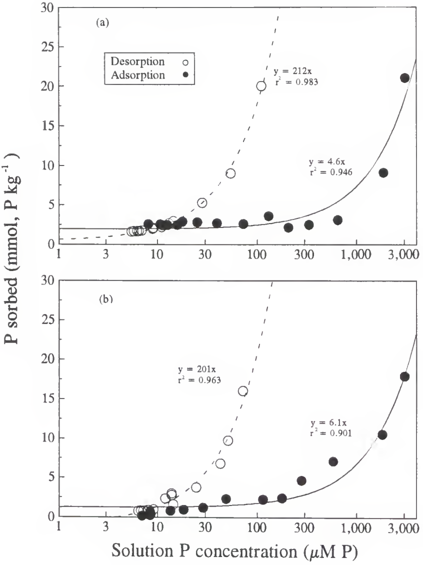

Fig. 4.4. Linear phosphorus sorption isotherms for Lake Apopka marsh soils (unamended) modified for native sorbed P according to Fitter and Sutton (1975), and desorbed P. (a) the soil before flooding, (b) the soil after 12 weeks of incubation.

Table 4.3. Phosphorus sorption parameters for unamended (Controls) and chemically amended Lake Apopka marsh soils.

Amended-soils	Rates	Linear Eq.		Langmuir Eq.			Freundlich Eq.		
		K_n	R^2	K_L	S_{max}	R^2	K_f	N	R^2
	g kg^{-1} soil	L kg^{-1}		L mmol^{-1} P,	mmol P kg^{-1}		L kg^{-1}		
Control-1	0	4.6	0.94	1.2	9.0	0.20	N.D	N.D	N.D
Control-2	0	6.1	0.90	1.6	18.4	0.85	1.0	0.65	0.92
$CaCO_3$	15.3	9.8	0.82	3.4	25.9	0.94	3.1	0.58	0.92
	102	12.8	0.75	3.8	33.1	0.97	28.0	0.61	0.93
$Ca(OH)_2$	11.3	10.3	0.86	2.0	29.1	0.91	1.8	0.66	0.93
	75	30.6	0.72	5.2	68.1	0.98	10.0	0.57	0.95
Dolomite	24.5	6.3	0.92	3.0	16.7	0.68	2.0	0.56	0.90
	175	10.2	0.70	4.0	26.2	0.95	5.4	0.50	0.97
$FeCl_3$	1.80	5.1	0.44	5.4	13.2	0.92	8.5	0.34	0.96
	11.8	15.0	0.81	2.7	41.8	0.92	4.0	0.59	0.97
Alum	14.5	14.3	0.94	1.3	43.6	0.70	1.8	0.67	0.95
	23.1	22.6	0.94	1.0	70.7	0.81	1.2	0.83	0.93
$CaCO_3/FeCl_3$	51+5.5	20.8	0.89	3.2	49.8	0.84	7.1	0.54	0.98
$CaCO_3$ /Alum	51+11.5	28.0	0.74	7.4	61.0	0.92	18.0	0.47	0.93

N.D. is not determined;

S_{max} is P sorption capacity in Langmuir equation; R^2 is coefficient determination; N is Freundlich constant; K_n, K_L, and K_f are Linear partition coefficient, Langmuir constant (related to binding capacity), and Freundlich partition coefficient, respectively.

Control-1: Lake Apopka marsh soil before flooding.

Control-2: Lake Apopka marsh soil after 12 weeks of flooding.

$Ca(OH)_2$ and the mixture of $CaCO_3$/alum showed significant increases in P sorption even at low P solution ($\leq 10\ \mu M$ P) (Fig. 4.5 d and Fig. 4.6 f). Desorption data for all soils were well fitted to the simple linear equation. The r^2 values of the linear desorption isotherms for all soils ranged from 0.98 to 0.99.

Phosphorus sorption capacity Phosphorus sorption capacity (S_{max}) of all chemically amended soils ranged from 13 to 71 mmol P kg^{-1} (Table 4.3). The control soil before flooding showed the lowest S_{max} values (9 mmol P kg^{-1}). The control soil after 12 weeks of flooding period has S_{max} value 18 mmol P kg^{-1}. The highest S_{max} was observed in the soil amended with alum (71 mmol P kg^{-1}). Similarly, the binding energy (K_L) also increased with application of chemical amendments. Soils amended with alum and $Ca(OH)_2$ and the mixture of $CaCO_3$/alum provided the highest capacity to retain P (Fig. 4.7 and 4.8). Among chemical amendments at lower rates, the S_{max} values for amended soils were as follows: alum (44, r^2=0.7) > $Ca(OH)_2$ (29, r^2=0.91) > $CaCO_3$ (25, r^2=0.94) > dolomite (17, r^2=0.68) > $FeCl_3$ (13, r^2=0.92) (Table 4.3).

Phosphorus desorption capacity Control 1 soil desorbed more P than P adsorbed in even high P solution concentrations, indicating a large pool of labile P. The high slope of linear regression equation for the control 1 soil (r^2=0.65) indicated that 99% of P adsorbed was desorbed (Fig. 4.7 a). Control 2 soil also showed that much of the P adsorbed was also desorbed (slope=0.86, r^2=0.98). All chemically amended soils showed increased capability of retaining adsorbed P. The soils amended with lime materials had lower slopes of linear regression equations than alum and $FeCl_3$ amended soils (Fig. 7 c, d, e, and f).

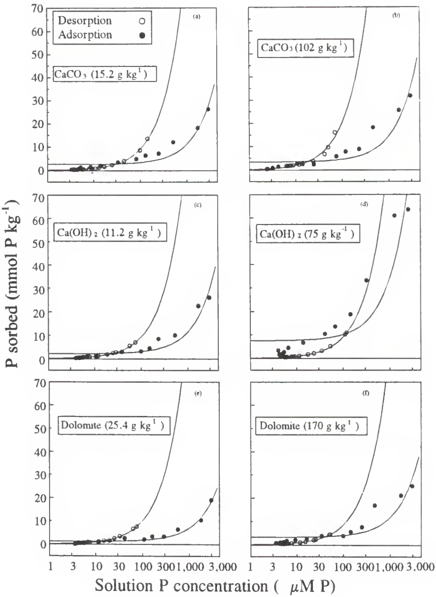

Fig. 4.5. Phosphorus sorption isotherms for soils amended with Ca materials modified for native sorbed P according to Fitter and Sutton (1975) and desorbed P. All chemically amended soils were air-dried after 12 weeks of incubation.

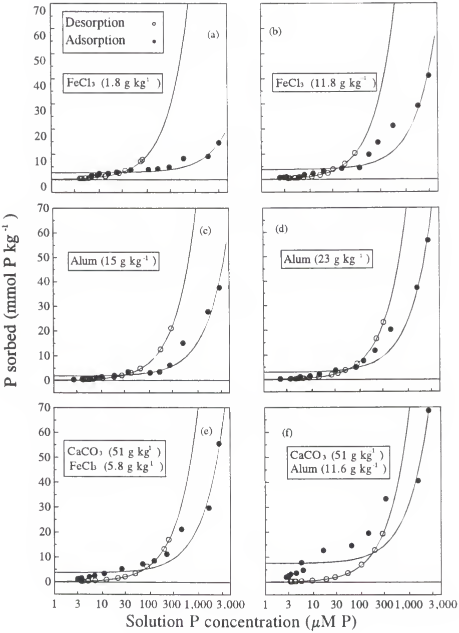

Fig. 4.6. Phosphorus sorption isotherms for soils amended with $FeCl_3$, alum, and mixtures ($CaCO_3/FeCl_3$ and $CaCO_3$/alum) amended soils modified for native sorbed P according to Fitter and Sutton (1975) and desorbed P. All chemically amended soils were air-dried after 12 weeks of incubation.

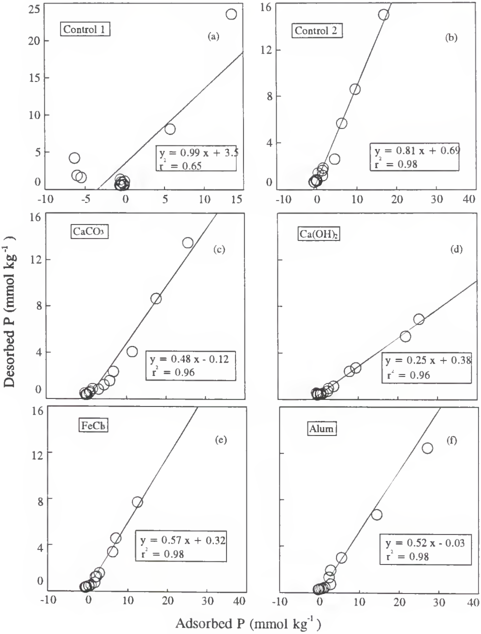

Fig. 4.7. Adsorbed P was plot with desorbed P for unamended and lower rated chemically amended soil. Control 1: Lake Apopka marsh soils before flooding, Control 2: Lake Apopka marsh soils after a 12-week of incubation, $CaCO_3$: 15.3 g kg^{-1}, $Ca(OH)_2$: 11.3 g kg^{-1}, $FeCl_3$: 1.8 g kg^{-1}, and alum: 14.5 g kg^{-1}.

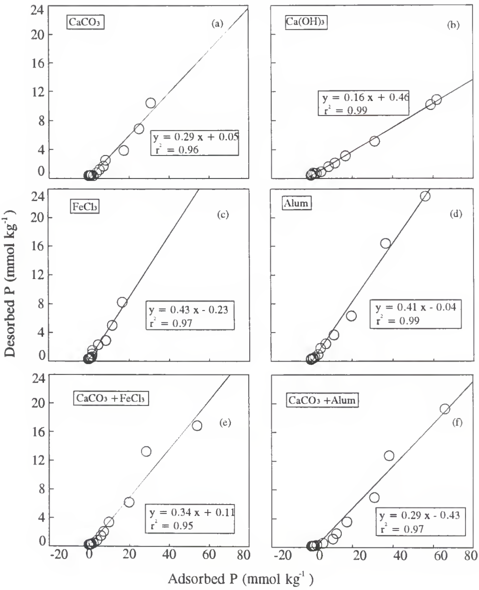

Fig. 4.8. Adsorbed P was plot with desorbed P for unamended and lower rated chemically amended soil. $CaCO_3$: 102 g kg^{-1}, $Ca(OH)_2$: 75 g kg^{-1}, $FeCl_3$: 11.5 g kg^{-1}, and alum: 23.5 g kg^{-1}, $CaCO_3$ + $FeCl_3$: 51+5.8, and $CaCO_3$ + alum: 51+11.8

Soil amended with $Ca(OH)_2$ had the lowest slope of linear regression equation (0.25) (Fig. 4.7 d), followed by $CaCO_3$, alum, and $FeCl_3$. Similar trends were observed in the amended soils at higher rate (Fig. 4.8). Capacities of retaining the P adsorbed for all chemically amended soils were shown to be greater at higher rates than lower rates of amendments.

Extractable cations.

Total Ca and Mg for control-2 was shown to be less than that of control-1(Table 4.4). The soils amended with lime materials ($CaCO_3$, $Ca(OH)_2$, and dolomite) resulted in increased water soluble Ca, HCl-extractable Ca, and total Ca as compared with control soils. Water soluble and KCl extractable Ca and Mg, however, showed poor linear relationships with total Ca and Mg, respectively, while HCl extractable Ca and Mg were linearly related ($r^2 > 0.99$) with total Ca and Mg, respectively (Fig. 4.9). In alum and $FeCl_3$ amended soils, water soluble Ca and Mg levels were increased, while exchangeable (KCl Ext.) and HCl-extractable Ca were decreased. Molar ratios of the water soluble Ca to Mg and HCl-extractable Ca to Mg in control soils were about 2:1 and 5:1, respectively. Both ratios increased in $Ca(CO)_3$ and $Ca(OH)_2$ amended soils, but decreased in dolomite amended soils.

The oxalate-extractable Fe and Al were higher than CDB-extractable Fe and Al in both amended and unamended soils (Table 4.5). In comparisons of the oxalate-extractable and total Al/Fe, the oxalate-extractable Al was much less than total Al, but the oxalate-extractable Fe was nearly equal to the total Fe. Aluminum extracted with the $CuCl_2$ solution from all the chemically amended soils ranged from 23 to 29 mmol Al kg^{-1}

Table 4.4. Extractable Ca and Mg in the unamended (Controls) and selected chemically amended Lake Apopka marsh soils used for this sorption test.

Amended-Soils	Amendment Rate	pH	Ca				Mg				Ca:Mg (water)	Ca:Mg (HCl) Ca+Mg	HCl
			water	KCl	HCl	Total	water	KCl	HCl	Total			
	g kg^{-1}		mmol kg^{-1}										
Control-1	0	4.7	8.0	490	930	992	4.2	128	179	189	1.9	5.2	1109
Control-2	0	5.9	7.5	475	916	971	3.6	124	176	183	2.0	5.2	1092
$CaCO_3$	15.2	6.7	15.1	529	1063	1093	6.0	117	172	178	2.5	6.2	1235
	102	7.5	45.2	530	1821	1896	15.0	96	157	168	3.0	11.6	1978
$Ca(OH)_2$	11.3	6.7	13.6	520	1073	1082	5.9	116	179	190	2.3	6.1	1252
	75	8.0	52.5	598	1803	1846	14.0	86	169	174	3.8	10.7	1972
Dolomite	25.4	6.6	8.8	440	1030	1052	6.2	150	316	336	1.4	3.3	1346
	170	6.9	16.5	400	1666	1686	12.6	149	1052	1143	1.3	1.6	2718
$FeCl_3$	1.8	5.7	13.3	473	911	925	6.9	123	177	182	1.9	5.2	1088
	11.5	5.5	32.4	462	905	920	19.0	120	186	183	1.7	5.2	1081
Alum	14.5	5.5	38.8	480	904	919	21.8	120	175	179	1.8	5.3	1079
	23.1	5.3	72.9	485	914	925	38.0	119	172	178	1.9	5.3	1086
$CaCO_3$ + $FeCl_3$	51 + 5.8	7.1	52.2	535	1453	1507	20.0	101	178	193	2.6	8.2	1631
$CaCO_3$ + Alum	51 + 11.5	7.2	79.0	585	1479	1511	25.8	101	174	187	3.0	8.5	1653

Control-1: Lake Apopka marsh soil before flooding.
Control-2: Lake Apopka marsh soil after 12 weeks of flooding.

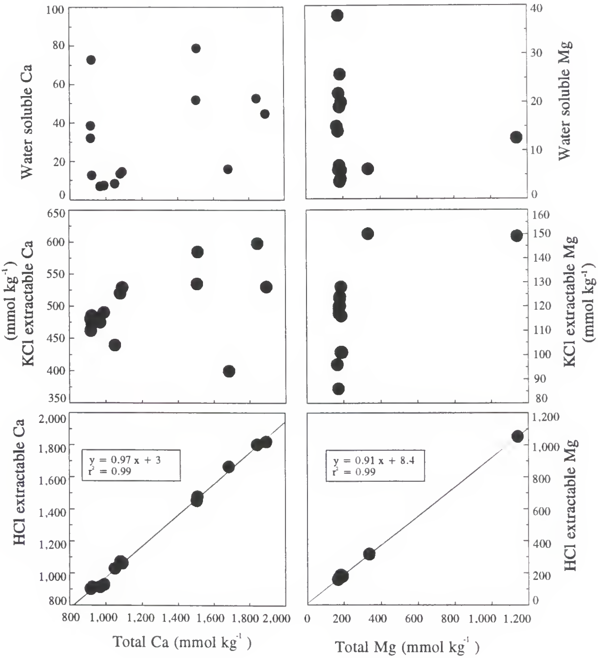

Fig. 4.9. Linear regression of water soluble, KCl-extractable, and HCl-extractable Ca and Mg concentrations versus total Ca and Mg concentrations.

Table 4.5. Various extractable Al and Fe in the unamended (Controls) and selected chemically amended Lake Apopka marsh soils used for this sorption test.

Amendment	Rate	pH	Al					Fe				Al:Fe (HCl)	HCl Al+Fe
			$CuCl_2$	Oxal	CDB	HCl	Total	Oxal	CDB	HCl	Total		
	g kg^{-1}		mmol kg^{-1}										
Control-1	0	4.7	29	44	38	40	106	91	50	66	100	0.63	106
Control-2	0	5.9	27	41	35	38	101	88	43	64	93	0.58	102
$CaCO_3$	15.2	6.7	27	42	34	39	99	82	40	63	86	0.62	102
	102	7.5	25	39	32	37	96	78	40	60	84	0.62	97
$Ca(OH)_2$	11.3	6.7	27	43	35	43	99	85	43	66	88	0.61	109
	75	8.0	28	41	33	41	96	77	41	63	85	0.67	104
Dlomite	25.4	6.6	25	41	33	38	64	82	41	63	87	0.60	101
	170	6.9	23	35	28	35	84	72	36	57	75	0.62	92
$FeCl_3$	1.8	5.7	27	42	34	38	99	89	42	64	99	0.59	102
	11.5	5.5	27	41	34	39	96	99	39	74	119	0.60	113
Alum	14.5	5.5	53	84	69	78	142	73	37	58	79	1.35	136
	23.1	5.3	72	115	93	103	172	68	33	54	73	1.89	157
$CaCO_3$ + $FeCl_3$	51 + 5.8	7.1	24	40	32	41	92	76	38	62	81	0.66	109
$CaCO_3$ + Alum	5.8 + 11.5	7.2	44	75	62	81	128	79	39	65	82	1.24	146

Oxal: ammonium oxalate; CDB: citrate-dithionite-bicarbonate

Control-1: Lake Apopka marsh soil before flooding.

Control-2: Lake Apopka marsh soil after 12 weeks of flooding.

except for the soils amended with alum and the mixture of $CaCO_3$/alum, which increased to 72 mmol Al kg^{-1}. The mole ratio of Al:Fe ranged from 0.53 to 0.67 for all soils except for the soils amended with alum and the mixtures of $CaCO_3$/alum, which had ratios in the range of 1.24 to 1.89. All extractable (CDB, oxalate, and HCl) Al and Fe, except CDB extractable Fe showed high regression relationships with total Al and Fe (Fig. 4.10).

Discussion

The low P sorption capacity of control-1 soil could be attributed to saturation of sorption sites, because of the large labile inorganic P pool resulting from past fertilization (Fig. 4.1). Low sorption characteristics and EPC_o values resulted in large P flux into floodwater, as was observed in previous experiments (Chapter 3). The control-2 soil also showed minimal P sorption capability in solutions with less than 150 μM P. These soils were flooded for 12 weeks, much of the labile inorganic P was removed as a result of flux from soil to floodwater. However, the capacity of control-2 soil in retaining P was significantly increased as compared with that of control-1 soil. Periodic flooding may contribute to the formation and maintenance of Al and Fe in noncrystalline (amorphous) form (Kuo and Mikkelsen, 1979). It was also believed that flooded and drained conditions caused transformation of crystalline normally stable crystalline Al and Fe minerals to noncrystalline form, increasing P sorption capacity (Kuo and Baker, 1982; Sah and Mikkelsen, 1988). Low Eh causes transformation of crystalline forms of Fe to amorphous forms, resulting in increased Fe concentrations as well as soluble P concentration in soil solutions during the flooding period. Increased amorphous Fe^{2+}

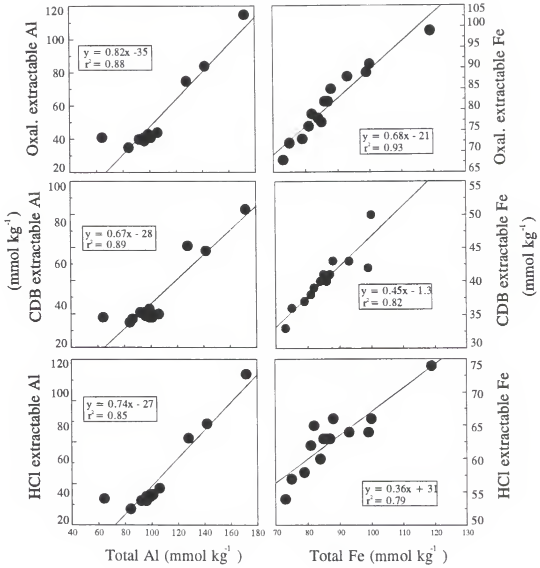

Fig. 4.10. Linear regression of all extractable Al and Fe (CDB, oxalate, and HCl Ext.) concentrations versus total Al and Fe concentrations.

probably oxidized to Fe^{3+} under the drained conditions and precipitated with P (Sah et al., 1989). Since Al do not undergo such a transformation, P bound to soil Al may be more resistance to changes induced by flooding. This could explain the stronger correlation observed between P sorption and oxalate-extractable Al than Fe (Table 4.6).

Lake Apopka marsh soil contained relatively high Ca, Mg, Al, and Fe concentrations (Table 4.1a). The previous fractionation study for Lake Apopka marsh soil (see Chapter 3) showed that the inorganic P fraction (about 50% of the total P) was almost evenly distributed into NaOH-RP (Fe- and Al-bound P) and HCl-RP (Ca- and Mg-bound P). This soil also showed higher oxalate-Fe/Al than CDB-Fe/Al, which would not be expected normally in noncalcareous soils (Table 4.5). Normally, CDB extraction is assumed to remove all free Al and Fe oxides, both crystalline and amorphous, while oxalate removes the amorphous fraction only (McKeague and Day, 1966; Mccalister and Logan, 1978). It is likely that most of the Fe extracted by CDB was oxalate-extractable and, in addition, oxalate may have extracted more Fe from Fe-carbonate and magnetite (Fe_3O_4) (Mccalister and Logan, 1978; Lindsay, 1979). The presence of magnetite would thus affect the relationship between oxalate-extractable Fe and P sorption capacity (Waldbridge and Struthers, 1993). Gamble and Daniels (1972) reported that magnetite was only sparingly soluble in CDB, while it had appreciable solubility in oxalate. These results suggested that relatively high concentration of metals might have controlled the soluble P in the Lake Apopka marsh, but P compounds formed in the soil may be some type of amorphous or no more than weakly crystalline complexes. Such complexes, when highly hydrated, has gel-like reactivity. The gel type of complexes has been

Table 4.6. Correlation coefficients (r) of P sorption parameters versus physico-chemical properties of the soils amended with alum and $FeCl_3$. n=8

parameters	pH	ws-P	S_{max}	Adsorbed-P	Total Desorbed P	K_L	K_f	EPC_o
pH								
ws-P	0.721							
S_{max}	0.935^{***}	-0.640						
Adsorbed P	-0.930^{***}	-0.735^{*}	0.957^{***}					
Total desorbed P	-0.591	0.044	0.760^{*}	0.695				
K_L	0.149	-0.317	-0.409	-0.273	-0.836^{*}			
K_f	-0.056	-0.500	-0.217	-0.078	-0.734^{*}	0.976^{***}		
EPC_o	0.488	0.933^{***}	-0.499	-0.586	0.065	-0.291	-0.434	
CDB-Fe	0.889^{**}	-0.880^{*}	0.911^{**}	0.902^{**}	-0.445	0.106	-0.097	-0.93^{*}
CDB-Al	-0.777^{*}	-0.379	0.854^{*}	0.672	-0.663	-0.513	-0.355	-0.254
Oxal-Fe	0.569^{*}	-0.318	0.658	0.435	-0.426	0.438	0.309	-0.268
Oxal-Al	-0.791^{*}	-0.405	0.862^{*}	0.683	-0.649	-0.485	-0.324	-0.276
$CuCl_2$-Al	-0.789^{*}	-0.397	0.862^{*}	0.684	0.659	-0.496	-0.337	-0.269
HCl-Al+Fe	-0.869^{*}	-0.459	0.928^{***}	0.792^{*}	-0.736^{*}	-0.505	-0.328	-0.301
HCl- Ca+Mg	0.677	0.961^{***}	-0.622	-0.736^{*}	-0.114	-0.181	-0.368	0.960
ws-Ca	0.945^{***}	-0.577	0.977^{***}	0.894^{**}	0.723	-0.371	-0.185	-0.041
% (desorbed/ adsorbed)	0.624	0.973^{***}	-0.617	-0.707	-0.058	-0.234	-0.400	0.985^{***}

Values marked with *, **, and *** are signuficant at the 5%, 1%, and 0.5% level respectively. CDB is citrate-dithionite-bicarbonate; Oxal is ammonium oxalate.

proposed as a major agent in P sorption by lake sediments since it has a very large reactive surface area with many sites for P retention when it was highly hydrated (Ryden, et al., 1972). Relatively high concentration of $CuCl_2$-extractable Al (more than 50 % of HCl-extractable Al) for all soils also indicated that organic P complexes with both Al and Fe (organic-Al-Fe-P) (Bloom, 1981) and/or organic acid (humic, fulvic, tannic and acetic acid Al)-P complexes (Sinha, 1971, Inskeep and Silvertooth, 1988) were expected to form (Table 4.5). Highly increased $CuCl_2$-extractable Al concentration (53 and 72 mmol kg^{-1}) in the soil amended with alum suggested that added Al were also complexed with organic matter in this soil.

The EPC_o value has been applied to predict P movement between the sediment and interstitial water (Green et al., 1978; Froelich, 1988; Olila, 1992). Since the floodwater P concentration of the Lake Apopka marsh was about 5 μM P, the high EPC_o (766 μM P) strongly suggests that these soils function as a source of P to overlying water. Depletion of labile P in control-2 soil, resulted in lower EPC_o, suggesting increased availability of sorption sites. Application of amendments increased P binding strength, resulting in lower EPC_o values. No P adsorption was observed for the control 1 soil until high concentration of P solutions ($>$ 60 mg L^{-1}) were added. Phosphorus adsorbed at high P concentration for control 1 soil was not retained in 0.01 M KCl solution. Linear regression equation for the soil indicated that 98 %($\pm$28) of P adsorbed could be desorbed (Table 4.7). Control 2 soil increased P sorption capacity (Table 4.3) and capacity of retaining P adsorbed as compared to the control 1 soil. Most of P adsorbed was desorbed (86%$\pm$4, r^2=0.96), however, in 0.01KCl solution of desorption test

Table 4.7. Linear regression equations used to estimate percent of P adsorbed. Adsorption versus desorption plot related to these equations are presented in Figs. 4.7 and 4.8. y: P desorbed, x: P adsorbed, a: slope

Amendments	Rate g kg^{-1}	y = a x	P-desorbed % of P adsorbed	r^2
Control-1	0	y = 0.98 x	98±28	0.32
Control-2	0	y = 0.86 x	86±4	0.96
$CaCO_3$	15.3	y = 0.48 x	48±2	0.96
	102	y = 0.29 x	29±1	0.96
$Ca(OH)_2$	11.3	y = 0.26 x	26±1	0.97
	75	y = 0.17 x	17±0.4	0.98
$FeCl_3$	1.8	y = 0.60 x	60±3	0.96
	11.5	y = 0.45 x	45±2	0.96
Alum	14.5	y = 0.52 x	52±2	0.98
	23.5	y = 0.41 x	41±1	0.99
$CaCO_3$ + $FeCl_3$	51+5.8	y = 0.34 x	34±2	0.96
$CaCO_3$ + alum	51+11.8	y = 0.28 x	28±1	0.96

Control-1: Unamended Lake Apopka marsh soil before flooding.

Control-2: Unamended Lake Apopka marsh soil after 12 weeks of incubation.

(Table 4.7). All chemically amended soils showed increased P sorption capacities as compared to controls. For examples, EPC_o and S_{max} were significantly increased by amending Lake Apopka marsh soil (Figs. 4.1, 4.2, and 4.3, and Table 4.3). Chemically amended soils also increased the capacities of retaining P adsorbed. Soil amended with $Ca(OH)_2$ retained 74% of P adsorbed and followed by $CaCO_3$ (48%), alum (52%), and $FeCl_3$ amendments (Table 4.7). Similar trends and increased capacities were observed in the higher rates as compared the lower rates of chemical amendments. Soil amended with $Ca(OH)_2$ at higher rate retained 83% of the P adsorbed. Soils amended with $CaCO_3$ and $Ca(OH)_2$ showed greater capacities of retaining P adsorbed than $FeCl_3$ and alum amendments. These results indicated that P adsorbed by the $CaCO_3$ and $Ca(OH)_2$ amendments was less soluble in KCl solution than P adsorbed by the alum and $FeCl_3$ amendments. Amount of P desorbed (100*[desorbed/adsorbed]) at each added P solution concentrations (not shown in this Chapter) indicated that percent P desorbed decreased significantly at 65 μM of the P solution added and then increased up to 55% and 65% with P solution concentrations higher than 65 μM for $CaCO_3$ and alum/$FeCl_3$ amended soils, respectively. It is believed that P is sorbed on high-energy sites at low P solution concentrations, while it is held on low energy sites at high P solution concentrations (Ryden and Syer, 1977). The soils of higher rates of amendments had less P desorbed than the soils with lower rates of amendments. This clearly indicated that chemical addition enhanced the P sorption capability of Lake Apopka marsh soil, and the P adsorbed was less soluble than native P in the soils. In higher rate of $Ca(OH)_2$ amended soils, 17% ($\pm$0.4) of the previously adsorbed P was desorbed. This may be attributed to coprecipitation of P with $CaCO_3$ (Otsuki and Wetzel, 1972) and discrete precipitation of beta-tricalcium and octacalcium phosphates (Ferguson, 1973). Carbonate mineral $CaCO_3$ (calcite) was detected in the soil amended with $Ca(OH)_2$ through X-ray diffraction analysis (see Chapter 3). In the calcite, P ions may replace water molecules, bicarbonate ions, and hydroxyl ions adsorbed on vacant coordinate positions of exposed surface Ca^{2+} ions. The relative adsorption strength of the phosphate ions to Ca^{2+} ions is higher than those of bicarbonate ions and hydroxyl ions to Ca^{2+} ions (Kuo and Lotse, 1972). In calcareous systems, formation of a surface P-complex on $CaCO_3$ that is believed to be later transformed into apatite (Stumm and Leckie, 1971). The solubility diagram for calcium P compounds also indicated that floodwater and porewater were supersaturated with respect to beta-tricalcium, octacalcium phosphates, and apatite. If hydroxyapatite and solid forms of Ca phosphate compounds were dominated in water systems, P concentration was supposed to be very low. Water soluble P concentrations in floodwater, however, were still high (see Chapter 3). This observation suggests that precipitation of solid phases was probably inhibited by presence of Mg (Marten and Harris, 1970), carbonate ions (Stumm and Leckie, 1971), and dissolved organic acids (Inskeep and Silvertooth, 1988). Formation of metastable surface complex, such as $Ca_2(HCO_3)_2HPO_4$, which was believed to be replaced later by a more stable compound $Ca_3(HCO_3)_3PO_4$ ($pK_{sp}=28.5$) was reported to control the solubility of P and $CaCO_3$ in the Jordan river (Yigal, et al., 1993).

Control soils showed two different slopes (low and high) in P sorption isotherms. Low and high slopes in P sorption isotherms responded to the a low and high P solution, respectively. It was believed that P sorption occurred after surpassing the EPC_0 level due to adsorption onto calcite or coprecipitation with Ca carbonates (Brown, 1980; Otsuki and Wetzel, 1973; Olila, 1992) and a discrete precipitation (Ferguson, 1973) was responsible for second high slope. Unamended soils (control-1 and control-2), however, gave no peaks of calcite as a calcium carbonate mineral and any P minerals in the X-ray diffraction analysis (see Chapter 3). Mechanism associated with dissolved P removal in acid soil are usually dominated by adsorption by Fe and Al oxides and clay minerals at lower solution P concentrations and by the precipitation of insoluble Fe and Al phosphates at higher concentrations (Walbridge and Struthers, 1993). This result may indicate that adsorption was the dominating mechanism taking place on various sites of the surface and in the layer of the surface, and/or amorphous forms (Ca, Al, and Fe) rather than crystalline forms were being nucleated and growing on the surface in the high P solution (Cole, 1953; Griffin and Jurinak, 1973).

Simple product moment correlations for the adsorption parameters versus selected chemical and physical properties were calculated for two groups of soil: 1) soils amended with lime materials ($CaCO_3$, $Ca(OH)_2$, and dolomite) (Table 4.6), 2) soils amended with alum/$FeCl_3$ (Table 4.8). The S_{max} of soils amended with lime materials was strongly correlated with 1M HCl-extractable (Ca+Mg) and water-soluble Ca, whereas the S_{max} were negatively correlated with CDB-extractable Al/Fe and oxalate-extractable Al/Fe.

Table 4.8. Correlation coefficients (r) of P sorption parameters versus physico-chemical properties of the soils amended with lime materials. n=8

Parameters	pH	ws-P	S_{max}	Adsorbed-P	Total Desorbed P	K_L	K_f	EPC_o
pH								
ws-P	-0.739^{*}							
S_{max}	0.891^{***}	-0.636^{*}						
Adsorbed P	0.934^{***}	-0.629^{*}	0.992^{***}					
Total desorbed P	-0.187	0.559	-0.048	-0.074				
K_L	0.919^{***}	-0.708^{*}	0.805^{**}	0.867^{***}	-0.115			
K_f	0.684^{*}	-0.447	0.430	0.494	0.143	0.537		
EPC_o	-0.520	0.943^{***}	-0.438	-0.491	0.587	-0.554	-0.285	
CDB-Fe	-0.564	0.80^{**}	-0.365	-0.455	0.417	-0.723^{*}	-0.350	0.840^{***}
CDB-Al	-0.541	0.599	-0.311	-0.396	0.292	-0.707^{*}	-0.384	0.638^{*}
Oxal-Fe	-0.766^{*}	0.673^{*}	-0.556	-0.637	0.251	-0.885^{***}	-0.497	0.606
Oxal-Al	-0.370	0.393	-0.162	-0.238	0.063	-0.555	-0.382	0.478
$CuCl_2$-Al	-0.236	0.436	0.094	0.001	0.409	-0.337	-0.309	0.557
HCl-Al+Fe	-0.242	0.247	0.026	-0.068	-0.106	-0.476	-0.418	0.339
HCl- Ca+Mg	0.633^{*}	-0.394	0.450	0.513	-0.027	0.736	0.486	-0.342
ws-Ca	0.916^{***}	-0.526	0.872^{***}	0.893^{***}	0.159	0.784^{**}	0.789	-0.289
% (desorbed/ adsorbed)	-0.649	0.982^{***}	-0.548	-0.604	0.622	-0.654	-0.349	0.981^{***}

* values marked with a *, **, and *** are significant at 5%, 1% and 0.5%, respectively.
CDB is citrate-dithionite-bicarbonate; Oxal is ammonium oxalate.

However, positive correlations of S_{max} with $CuCl_2$-extractable Al and HCl-extractable Fe/Al was also shown (Table 4.6). These observations demonstrate, as would be expected, that P sorption in soils amended with lime materials was regulated mainly by Ca and Mg. Relatively high amount of Al and Fe in the soil, however, may play a minor role in P sorption. Organically bound Al probably is also involved in P sorption (Hargrove and Thomas, 1981; Bloom, 1981, and Inskeep and Silvertooth, 1988). The S_{max} was positively correlated with adsorption energy (K_L), which indicates that as the P sorption capacity increases, adsorption energy increases (Green et al., 1978). The K_L was negatively correlated with the total P desorbed and EPC_o, indicating that as adsorption energy increases, P is held more tenaciously and is less likely to be released.

A positive correlation of EPC_0 with both CDB-extractable Al/Fe and oxalate-extractable Al/Fe suggests that relatively high concentrations of Al and Fe in the soils amended with lime materials can cause high EPC_0 values. It may be explained with increased pH by liming soil resulted in high concentrations of CDB- and oxalate-extractable Al/Fe, releasing native P. The S_{max} for the soils amended with lime materials at lower rates ranged from 17 to 29 mmol kg^{-1}, whereas the S_{max} for the higher rates application ranged from 26 to 68 mmol kg^{-1} (Table 4.4). These S_{max} values were comparable to those of lake sediments, which was the highest (27-40) among the sediments of Lake Okeechobee (Olila, 1992).

The S_{max} and adsorbed P of the alum/$FeCl_3$ amended soils were positively correlated with both CDB/oxalate-extractable Al/Fe and HCl-extractable Al/Fe, whereas the S_{max} was negatively correlated with HCl-extractable Ca/Mg (Table 4.8). The results, as would be expected, indicated that the added Al and Fe was responsible for P sorption in the amended soils. The importance of oxalate-extractable Fe as a major contributor for P sorption of noncalcareous soils has been previously reported (Hsu, 1964; Khalid et al., 1977; Green et al., 1978; Mccallister and Logan, 1978). Shukla et al. (1971) also reported that removal of oxalate-extractable Fe from soils virtually eliminated the capacity of P sorption. The positive correlation among the S_{max}, CDB/oxalate-extractable Fe/Al, and HCl-extractable Al/Fe, and the positive correlation between CDB/oxalate-extractable Fe/Al and HCl-Al/Fe, and total desorbed P, may explain that noncrystalline forms of Al-Fe compounds were actively involved in P sorption. Negative correlations between K_L and EPC_o, and K_L and total desorbed P, and a positive correlation between EPC_o and total desorbed P were observed. The implication is that both EPC_o and total desorbed P were probably controlled by the stability or energy of the phosphorus-colloid complex (Ryden, 1972; Mccalister and Logan, 1978).

Conclusions

Phosphorus sorption capacity of highly organic marsh soil was improved by amending it with chemical amendments. Phosphorus sorption capacity (S_{max}) of soils amended with lime materials was as follows: dolomite < $CaCO_3$ < $Ca(OH)_2$. The S_{max} was associated positively with HCl-extractable (Ca+Mg) and considerably high with $CuCl_2$-extractable Al, while it was also positively but weakly correlated with HCl-extractable Al/Fe. Phosphorus adsorption and desorption were linearly increased with the increased P solution concentrations. The desorption percent for the soil amended with $CaCO_3$ was significantly reduced at 65, 129, and 194 μM of P solutions and then increased up to 55% at higher P concentrations, while it remained less than 10 to 30% at all high P solution concentrations for the soil amended with $Ca(OH)_2$.

Soils amended with alum showed more P sorption capacity than soils amended with $FeCl_3$. The S_{max} for the alum amended soils was even higher than those for $Ca(OH)_2$ amended soils. Desorption percent for the soils amended with alum and $FeCl_3$, however, was higher than the soils amended with lime materials. This information suggests that Al and Fe-bound P formed in the soils by alum and $FeCl_3$ treatment were more soluble than Ca-bound P formed in the soils by lime treatments. The S_{max} for alum and $FeCl_3$ amended soils were correlated with oxalate/CDB-extractable Fe/Al, indicating that P sorption by the soils was regulated mainly by Al and Fe components.

The P sorption data for the $FeCl_3$ and alum amendments were best fit to the Freundlich equation, whereas P sorption isotherm for lime based amendments was better described by both the Langmuir and Freundlich equations. Unamended Lake Apopka marsh soils were best fit to the simple linear isotherm.

Net P sorption for Lake Apopka marsh soil (control-1) was not observed until P concentration exceeded the EPC_o (766 μM P) level. The EPC_o for Control-2, once used for 12 weeks of the column incubation study, was significantly reduced to 18 μM P. Flooding and draining conditions of control-2 provided more amorphous chemical species, which was believed to precipitated with newly added P. The high EPC_o, percentage P desorbed (total desorbed P/adsorbed P excluding native P), slightly acidic condition, and relatively high amount of oxalate-extractable Fe/Al for the Lake Apopka marsh soil indicated that both noncrystalline Ca/Mg and Al/Fe P compounds or the mixed Ca-bound P with Al/Fe bridged with organic acids may be responsible for controlling P. Capabilities of chemically amended soils in retaining sorbed P are in the order of : $Ca(OH)_2$ > $CaCO_3$ > alum > $FeCl_3$ > controls, while S_{max} values are in the order of: alum > $Ca(OH)_2$ > $CaCO_3$ > $FeCl_3$ > controls.

CHAPTER 5
INFLUENCE OF REDOX POTENTIAL ON PHOSPHORUS SOLUBILITY IN CHEMICALLY AMENDED LAKE APOPKA MARSH SOILS

Introduction

The solubility and reactivity of different forms of phosphorus (P) in wetland soils are influenced by physical, chemical and biological characteristics of the system. Among other factors, temperature (Holdren and Armstrong, 1980), pH (Mayer and Kramer, 1986), Eh (Moore et al., 1991), interstitial soluble P level (Kamp-Nielsen, 1974), and microbial activity have been reported to regulate P solubility in soil-water systems. The effect of redox potential (Eh) on P solubility was studied in the early work by Mortimer (1941), who demonstrated that P release from sediment was greater when the overlying water was anoxic as a result of the reduction of relatively insoluble ferric phosphate. The influence of redox potential on P reactivity was reported for noncalcareous sediments that contain abundant transitional metals, especially iron and manganese (Holdren and Armstrong, 1980; Nealson and Saffarini, 1994; Moore and Reddy, 1994).

Phosphate apparently precipitates as Fe^{3+}-, Mn^{4+}-, and Al-phosphates under aerobic conditions in noncalcareous soils (Ponnamperuma, 1972). Under subsequent reducing conditions, dissolved reactive phosphorus (DRP) is released to the interstitial water from soil Fe^{3+}- and Mn^{4+}- phosphates due to the reduction of Fe^{3+} and Mn^{4+} to more soluble Fe^{2+} and Mn^{2+} forms, respectively. The critical Eh for Fe^{3+} reduction was found to be between 300 mV and 100 mV at pH 6 and 7, -100 mV at pH 8, and 300 mV at pH 5 (Gotoh and Patrick, 1974; Patrick and Henderson, 1981). Under oxidized conditions, strengite and trivalent Mn phosphate would be dominant, whereas vivianite and reddingite would govern the behavior of P under reduced soil conditions (Emerson and Widmer, 1978; Moore et al., 1991). Ferrosoferric hydroxyphosphates have been reported to be stable minerals under oxidized conditions (Nriagu and Dell, 1974).

In calcareous systems, apatite equilibrium may control P solubility. However, apatite formation may be hindered by the presence of carbonate (Stumm and Leckie, 1970), a high Mg concentration (Martens and Harriss, 1970), and organic acids (Inskeep and Silvertooth, 1988). Cole et al. (1953) reported that amorphous Ca compounds rather than crystalline Ca compounds controlled P concentration in soil solutions containing a high potential of Ca and P. The reaction of P with calcite has been reported as adsorption on the calcite surface or seed crystal (Griffin and Jurinak, 1973) and/or coprecipitation of P with $CaCO_3$ (Otsukie and Wetzel, 1972). The solubility of Ca-bound phosphates such as apatite, beta-tricalcium phosphate, octacalcium phosphate, brushite, and monetite is controlled by pH rather than Eh.

High partial pressure of CO_2 tends to decrease pH and increase P solubility in soils having high levels of calcium-bound phosphates and organic matter. The solubility of P in Lake Apopka marsh soil is dependent on both pH and Eh due to the reactions of P with Ca and Fe and Al. In an earlier study (Chapter 3), phosphorus fractionation of Lake Apopka marsh soils showed that HCl-bound P was lower than that of NaOH-bound P, suggesting that Fe and Al may be controlling P solubility. As shown in Chapter 3, the physico-chemical properties of Lake Apopka marsh soil changed significantly when treated various chemicals such as $CaCO_3$, alum, and $FeCl_3$. The soils amended with

$CaCO_3$ became more alkaline, whereas the alum/ $FeCl_3$ amended soils became more acidic.

It was hypothesized that changes in Eh may control P concentrations in chemically amended soils. The objectives of this study were 1) to evaluate the influence of Eh on P solubility in chemically amended soils and 2) to determine the solid phases regulating P solubility at different Eh levels in chemically amended marsh soils.

Materials and Methods

Soil Preparation

Bulk samples were obtained from Station 5 (Fig. 5.1) of the Lake Apopka marsh, air-dried and stored at the 4°C until used in the experiments. Soil slurry was prepared by mixing the air-dried soil samples with known aqueous concentrations of $CaCO_3$, $FeCl_3$, and alum at the rates of 15.3 g kg^{-1}, 1.8 g kg^{-1} and 14.5 g kg^{-1}. These amendment rates were found to be effective in immobilizing water-soluble P in these soils (see Chapter 3). The slurries were then air-dried, mixed, and transferred into 2-L flasks.

Experimental Setup

Duplicate sets of 2-L flasks (Fig. 5.2) were set up in the laboratory. Each flask was filled to the 1.8 L mark with the soil suspensions which were made up of air-dried soil slurries and deionized and distilled (DDI) water. The ratio of soil to DDI water was 1:20 (w/v). At the beginning of the experiment, air was bubbled through soil suspensions to obtain oxidized conditions. Redox potential and pH were closely monitored using an electrical data logger equipped with CL-10 software and a Cole-Parmer pH controller, respectively.

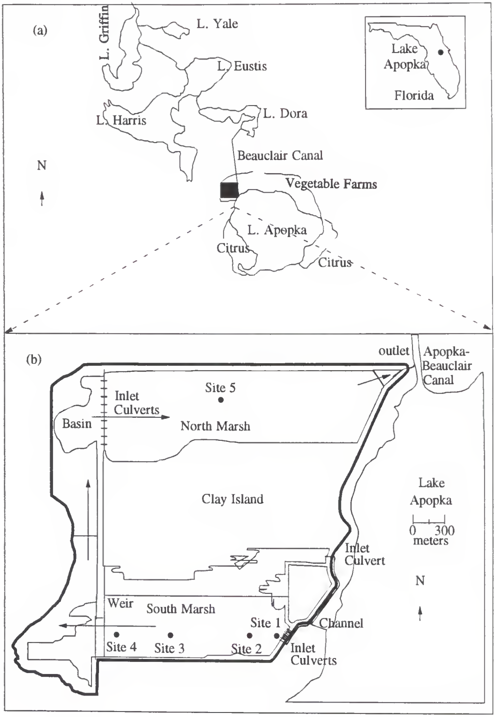

Fig. 5.1. (a) Oklawaha river basin, (b) Flow-way of the created wetland adjacent to Lake Apopka. Soil was obtained from Site 5.

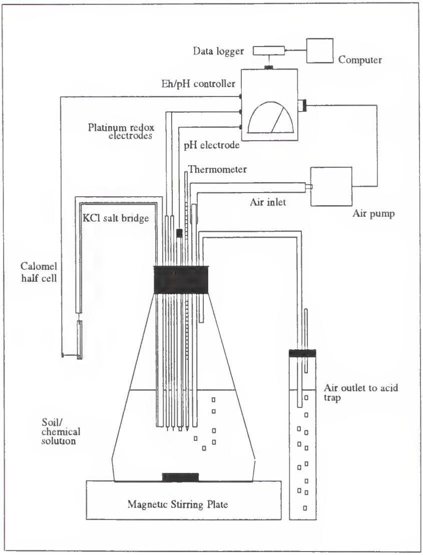

Fig. 5.2. Diagram illustrating the apparatus used in controlling redox potential (Eh) of chemically amended Lake Apopka marsh soils mixed with deionized and distilled water (DDI).

After 20 days, N_2 gas (balanced with 300 ppm CO_2) was introduced into the suspension to create an anaerobic condition. The suspensions were stirred continuously throughout the incubation period. After about 112 days, when Eh level decreased to -200 mV and a steady anaerobic condition was established, air was introduced again to create aerobic conditions.

When stable Eh levels of 400, 200, 0, -100, 0, 200, and 350 mV were attained, duplicate samples of soil suspension were withdrawn for soil characterization such as water content, pH, and dissolved reactive P (DRP) in porewater. The samples were also analyzed for KCl-extractable P, NaOH-extractable P, and HCl-extractable P according to the modified inorganic P fractionation scheme proposed by Hieltjies and Lijklema (1980). The soil suspensions were also analyzed for dissolved cations, oxalate and CDB-extractable Fe and Al, and 1 M HCl and KCl extractable Ca and Mg.

Analytical Methods

Dissolved reactive P (DRP) in all extracts was determined by the ascorbic acid method (Murphy and Riley, 1962) using an autoanalyzer (Technicon AA II). Soil TP was determined by the ignition method (Saunders and Williams, 1955). Four hundred milligrams (oven-dried) of soil was weighed into a 50 ml beaker and heated to 200°C in a muffle furnace. The temperature was then increased to 550°C. After 4 hours, samples were allowed to cool down to 200°C and removed from the furnace. The sample was then moistened with distilled water and 20 ml of 6 M HCl was added, and the mixture was slowly evaporated to dryness on a hot plate at low temperature. The residue was dissolved in 2.5 ml 6 M HCl at near boiling point and filtered (Whatman # 41). The filtrate was diluted to 50 ml and stored at 4°C until analyzed for P (Murphy and Riley, 1962). This procedure was also used in determining residual total P obtained during the P fractionation.

The soils were analyzed for water-soluble and 1M HCl-extractable Ca, Mg, Al, and Fe. Total metals were determined by the ignition method. The metals were analyzed using an inductively coupled argon plasma emmission spectrometer (Thermo Jarrell Ash ICAP 61E; Franklin, MA). Electrical conductivity and dissolved inorganic C (DIC) of soil porewater were measured by using a conductivity meter (YSI model 31) and TOC analyzer (DC-190 ASM, Dohrmann), respectively.

Results

Physico-Chemical Properties of Sediments

Lake Apopka marsh soil was slightly acidic pH (5.9) and had a total P content of about 18 mmol kg^{-1} (Table 5.1). Ash content (weight basis) for all soils ranged between 13 and 15%, while water contents were from 54 to 57%.

Total Ca of the soil was 1155 mmol kg^{-1}, 36 to 42% of which was exchangeable (1M KCl). Total Al and Fe contents ranged between 96 to 150 mmol kg^{-1} each and > 90% of added Ca, Fe, and Al were extracted by 1M HCl. One mole HCl extracted approximately 86% of the total Ca, 41% of total Al, and 60% of total Fe. Added Ca, Al, and Fe as $CaCO_3$, alum, and $FeCl_3$ were well recovered (97, 91, and 99%, respectively) by 1 M HCl extracts. Concentrations of CDB extractable Al and Fe were lower than oxalate-extractable Al/Fe. The $CuCl_2$-extractable Al in alum treated soil had

Table 5.1. Selected physical and chemical properties of Lake Apopka marsh soil and chemically amended soils.

Properties		Control	$CaCO_3$	Alum	$FeCl_3$
pH		5.9	7.0	5.4	5.6
% water		59	56	54	57
% Ash		13	15	14	15
Total P		17.6	17.9	17.9	17.9
		-----------	---------------	mmol kg^{-1}--------	---------
P Fractions: 1 M KCl-RP		0.72	0.48	0.37	0.61
0.1 M NaOH-RP		3.18	3.73	4.87	6.20
0.5 M HCl-RP		3.34	3.88	4.24	4.31
Residual-P		8.47	8.98	8.03	7.10
% recovery		89	95	98	102
Total Metals	Ca	1155	1303(106*)	1045	1126
	Mg	213	192	179	195
	Al	100	102	150(116*)	96
	Fe	126	118	106	139(117*)
	Mn	5.1	3.1	3.0	3.0
1M KCl Extractable	Ca	416	475	438	442
	Mg	119	115	122	125
	Al	0	0	0	0
	Fe	0.09	0.09	0.07	0.11
	Mn	0.1	0.06	0.25	0.24
1M HCl Extractable	Ca	996	1158(97*)	1004	1013
	Mg	193	204	198	204
	Al	42	43	81(91*)	43
	Fe	76	76	75	87(99*)
	Mn	3.32	3.39	3.33	3.46
CDB Extractable	Al	26.4	27.0	54.7	28.5
	Fe	31.3	32.2	33.8	39.1
Oxalrate Extractable	Al	41.1	42.5	87.2	42.6
	Fe	88.6	89.7	92.9	102
0.5 M $CuCl_2$ Extractable	Al	20.2	20.8	46.3	21.8

Soils were amended with 15.3 g kg^{-1} as $CaCO_3$, 14.5 g kg^{-1} as alum, and 1.8 g kg^{-1} as $FeCl_3$.

* indicates recovery percent expressed as percent of added metals.

twice (46.3 mmol kg^{-1}) as compared to other soils.

Redox Potential and pH

Oxidizing conditions maintained a redox potential $>$ 400 mV after 21 to 25 days of aeration (Figs. 5.3, 5.4, 5.5, and 5.6). When N_2 gas was introduced it took about 6 to 7 weeks for the system to reach an Eh of 200 mV. Highly reducing conditions (Eh = -100 mV) were not established until another 6 weeks of continuous bubbling with N_2. Decreases in Eh were more rapid (3 to 4 weeks) to reach 200 mV for the $CaCO_3$ amended soils than the other treatments (Fig. 5.4).

Soil pH levels were about 5.5 for the control and those treated with alum and $FeCl_3$, whereas the soil amended with $CaCO_3$ had pH 7.0. Soil pH generally decreased under aerobic conditions, and increased under anaerobic conditions.

Dissolved Metals and Nitrate-N

The concentrations of water soluble Ca and Mg increased with time of incubation for all soils (Table 5.2). The soils amended with $CaCO_3$ had the lowest dissolved Ca and Mg concentrations in porewater, whereas alum amended soils had the highest dissolved Ca and Mg concentrations. Nitrate-N was detectable only under oxidized conditions (Eh $>$ 369 mV). Water soluble Fe concentrations were inversely related to Eh.

Forms of Soil Phosphorus

Inorganic P in soil accounted for about 41% of total P. Calcium-bound P (HCl-extractable P) levels were slightly higher than levels of Al/Fe-bound P (NaOH-extractable P). Chemically amended soils ($CaCO_3$, alum, and $FeCl_3$) had higher concentrations of HCl-extractable P and NaOH-extractable P fractions than the control (Table 5.1).

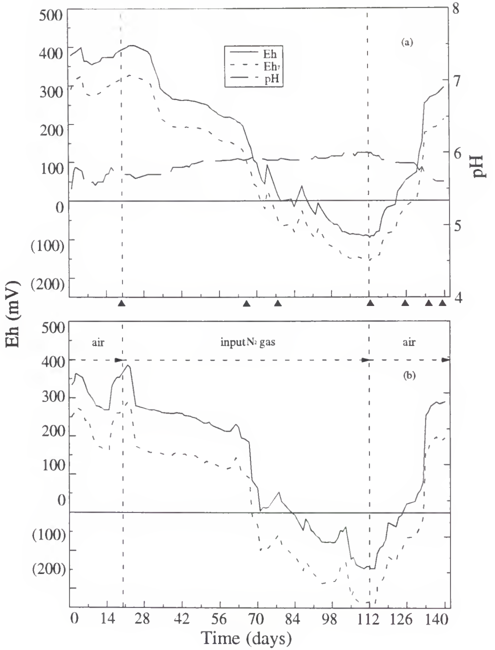

Fig. 5.3. Eh and pH changes versus incubation time on unamended Lake Apopka marsh soil (Control). Duplicated reactors (a and b) were filled with air-dried control soil and distilled and deionized water and cycled aerobically and anaerobically. Closed triangles indicate sampling time.

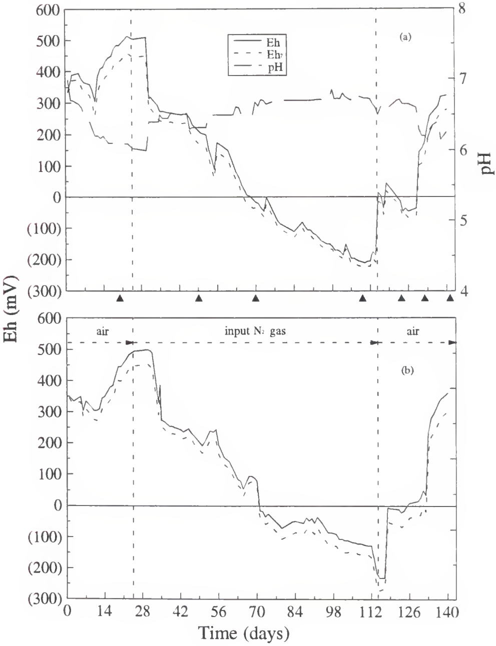

Fig. 5.4. Eh and pH changes versus incubation time on $CaCO_3$ amended soil. Duplicated reactors (a and b) filled with $CaCO_3$ amended soil and distilled and deionized water were cycled aerobically and anaerobically. Closed triangles indicate sampling time.

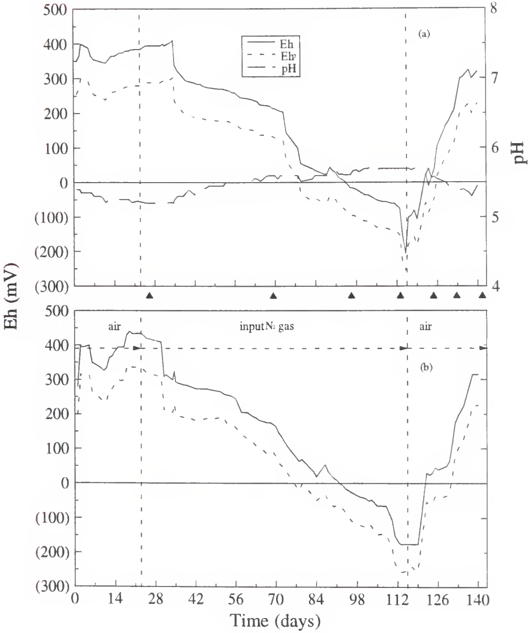

Fig. 5.5. Eh and pH changes versus incubation time on alum-amended soil. Duplicated reactors (a and b) filled with alum-amended soils and distilled and deionized water were cycled aerobically and anaerobically. Closed triangles indicate sampling time.

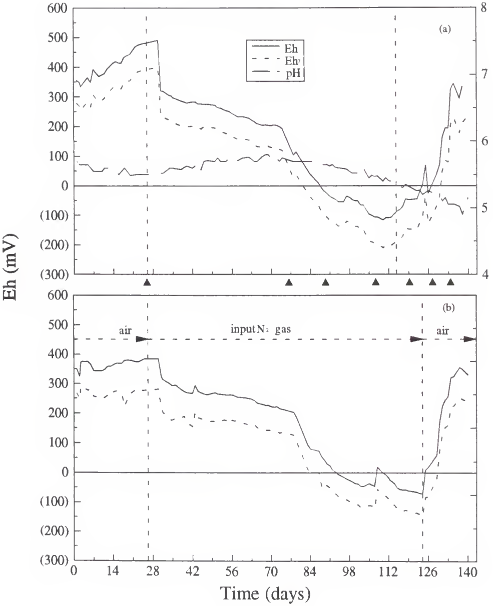

Fig. 5.6. Eh and pH changes versus incubation time on $FeCl_3$ amended soil. Duplicated reactors (a and b) filled with $FeCl_3$ amended soils and deionized and distilled water were cycled aerobically and anaerobically. Closed triangles indicate sampling time.

Table 5.2. Dissolved metals and nitrate concentrations in Lake Apopka marsh soil (Control) and chemically amended soils at different Eh levels.

Amended soils	Eh	pH	Water-Soluble Concentration (μM)					
(rate, g kg^{-1})	(mV)		Ca	Mg	Mn	Al	Fe	NO_3
Control	377	5.63	895	528	0.2	11	6.6	1553
	194	5.65	2134	1147	4.6	18	32	0
	-18	5.55	2619	1422	4.5	5.5	58	0
	-110	5.67	3390	1819	4.7	7.0	93	0
	-14	5.68	3528	1892	4.7	9.0	88	0
	199	5.64	3447	1865	3.6	5.4	4.0	0
	300	5.43	4803	2546	5.2	11	3.4	1304
$CaCO_3$	370	6.67	1010	494	0.4	8.4	6.4	1633
(15.3)	193	6.65	1389	592	1.9	18	17	0
	12	6.62	1732	691	4.5	20	52	0
	-124	6.12	1879	858	2.7	6.6	22	0
	-20	5.90	2013	910	2.7	13	14	0
	195	5.56	2262	1050	3.0	5.6	8.0	18
	320	5.43	2718	1250	3.0	5.6	3.2	1098
Alum	399	5.45	2981	1689	0.8	7.4	2.9	1662
(14.5)	205	5.65	3468	1817	8.6	11	51	0
	-15	5.61	3625	1890	8.8	8.3	82	0
	-114	5.70	3904	2014	9.1	12	97	0
	12	5.60	4241	2177	9.4	22	88	0
	204	5.45	4154	2164	7.9	9.2	4.4	0
	334	5.36	3890	2064	5.0	7.2	3.3	1361
$FeCl_3$	369	5.51	1324	815	0.4	7.4	8.9	1484
(1.8)	178	6.17	2162	1190	4.3	3.7	36	0
	-8	5.55	2303	1261	4.4	3.7	62	0
	-95	5.59	3219	1732	4.7	11	109	0
	-3	5.30	3130	1693	4.3	7.0	91	0
	216	5.27	3158	1731	3.4	5.4	3.0	0
	362	5.16	4701	2431	9.1	11	3.4	1316

Dissolved reactive P (DRP) concentrations were higher under reduced conditions than those under oxidized conditions for all soils (Fig. 5.7). Similar trends in DRP changes were observed in unamended and $FeCl_3$ amended soils (Figs. 5.7 a, d). Dissolved P concentrations were substantially low in alum and $CaCO_3$ amended soils under reduced conditions, as compared to control and $FeCl_3$ amended soils (Fig. 5.7 b, c).

In unamended soil, reducing conditions ($<$ 200 mV) increased the KCl-RP (reactive P) fraction, whereas both NaOH-RP and HCl-RP fractions were decreased between 400 and -100 mV (Fig. 5.8). In $CaCO_3$ amended soil, reducing conditions had minimal effect on the KCl-RP fraction, and the NaOH-RP fraction decreased with decreased Eh and increased with increased Eh (Fig. 5.9). The KCl-RP fraction of the alum/$FeCl_3$ amended soils decreased with an increase in Eh values. The NaOH-RP fraction for alum amended soils remained constant at Eh values $\leq$ 200 mV, and subsequent increases in Eh increased the NaOH-RP pool. (Fig. 5.10). However, the $FeCl_3$ amended soils had large changes in the NaOH-RP fraction with the different Eh levels (Fig. 5.11). The HCl-RP fractions of the $FeCl_3$/alum amended soils also decreased under reduced conditions and increased under oxidized conditions. In general, Ca-bound P (HCl-RP fraction) dominated in all soils both under reduced and oxidized conditions, whereas Al/Fe-bound P (NaOH-RP fraction) was major inorganic P under oxidized conditions. Dissolved reactive P (DRP) in porewater of the control was less than 5 and 31% of total P under aerobic and anaerobic conditions, respectively, while the NaOH-RP fraction was decreased from 16% under aerobic conditions to 2 % under anaerobic conditions. Soils amended with $FeCl_3$

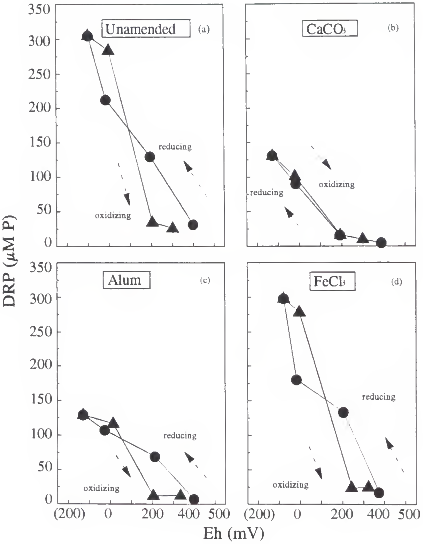

Fig. 5.7. Effect of Eh on dissolved reactive P in porewater of chemically amended Lake Apopka marsh soils. (a) unamended soil, (b) $CaCO_3$ amended soil, (c) alum amended soil, and (d) $FeCl_3$ amended soil.

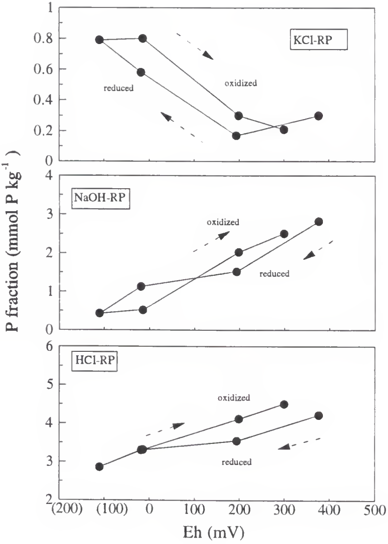

Fig. 5.8. Phosphorus fractions of unamended Lake Apopka marsh soil, as influenced by Eh changes. KCl-RP is loosely bound P; NaOH-RP is Al/Fe bound P; HCl-RP is Ca/Mg bound P.

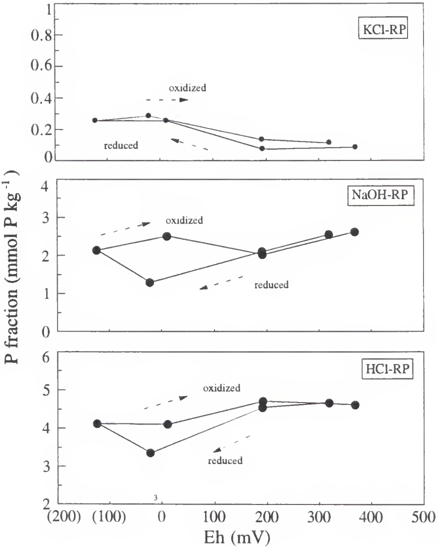

Fig. 5.9. Phosphorus fractions of $CaCO_3$ amended soil, as influenced by Eh changes. KCl-RP is loosely bound P; NaOH-RP is Al/Fe-bound P; HCl-RP is Ca/Mg-bound P.

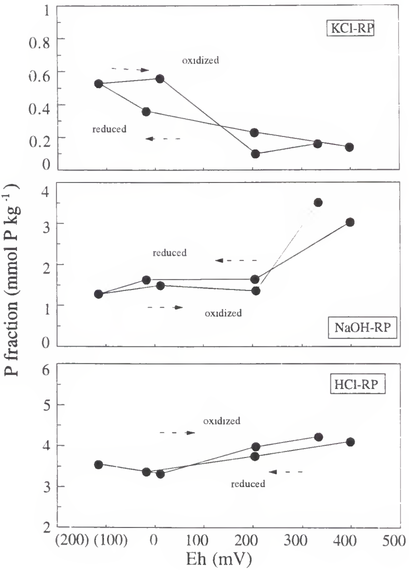

Fig. 5.10. Phosphorus fractions of alum-amended soil, as influenced by Eh changes. KCl-RP is loosely bound P; NaOH-RP is Al/Fe-bound P; HCl-RP is Ca/Mg-bound P.

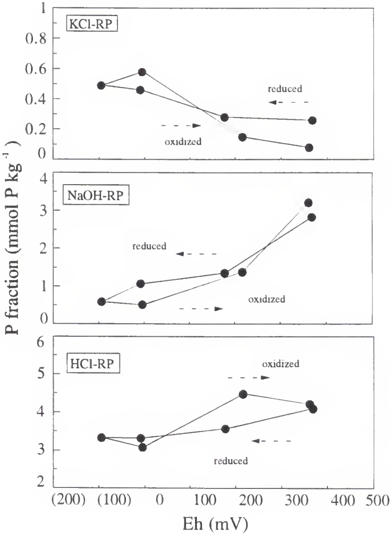

Fig. 5.11. Phosphorus fractions of $FeCl_3$ amended soil, as influenced by Eh changes. KCl-RP is loosely bound P; NaOH-RP is Al/Fe-bound P; HCl-RP is Ca/Mg-bound P.

responded more sensitively to Eh changes than unamended soil but with the same patterns in changes of DRP and NaOH-RP. Dissolved reactive P under aerobic conditions was only 1% of total P, whereas DRP under anaerobic conditions of porewater for soils amended with $CaCO_3$ and alum was 20% of total P. Aluminum/Fe-bound P (NaOH-RP) of the soils was about 17% and 7% of total P under aerobic and anaerobic conditions, respectively (Table 5.3). This P fractionation study also showed that NaOH-RP was much less than HCl-RP fraction for all soils, which was different from the results of the P fractionation study conducted for soil physico-chemical properties (Table 5.1). Information obtained from two P fractionation studies may indicate that DRP in porewater was attributed mainly to the NaOH-RP and to a less degree to HCl-RP.

Extractable Cations

Dissolved Fe concentrations in unamended soils gradually increased as the soil Eh decreased, followed by rapid decreases at Eh of 200 mV when soils subsequently were oxidized (Fig. 5.12 a). The $FeCl_3$ amended soil showed similar results to unamended soil, except for a higher dissolved Fe concentration at -100 mV (Fig. 5.12 d). Significant increased dissolved Fe concentration in alum amended soils were also observed at Eh 0 mV (Fig. 5.12 c). In $CaCO_3$ mended soil, dissolved Fe concentrations were lower than those in any other soils under reduced conditions, andalterations in Eh had minimal effect. The highest Fe concentration occurred at 0 mV, and decreased at -100 mV (Fig. 5.12 b).

Redox potential had no effect on HCl-extractable Ca, Mg, and Al concentrations in all soils. Dissolved Ca and Mg in all soils increased regardless of Eh changes (Table

Table 5.3. Inorganic P fractions of unamended (Control) and chemically amended Lake Apopka marsh soils at different redox potential (Modified Hieltjes and Lijklema, 1980 scheme).

Amended Soils ($g\ kg^{-1}$)	Eh	DRP	KCl-RP	NaOH-RP	HCl-RP	Residual P	Recovery	Total P
	mV	μM	---------	mmol kg^{-1}	---------	----------	%	mmol kg^{-1}
Control	377	30 (4.9)	0.30 (1.7)	2.83 (16)	4.22 (24)	7.34 (42)	89	17.3
	194	135 (16)	0.17 (1.0)	1.52 (8.8)	3.55 (21)	7.01 (41)	88	
	-18	193 (25)	0.58 (3.4)	1.13 (6.5)	3.31 (19)	5.76 (33)	87	
	-110	247 (31)	0.79 (4.5)	0.43 (2.5)	2.86 (17)	6.91 (40)	95	
	-14	135 (16)	0.80 (4.6)	0.52 (3.0)	3.32 (19)	8.74 (51)	94	
	199	33 (5.4)	0.30 (1.7)	2.03 (12)	4.12 (24)	11.0 (63)	105	
	300	26 (3.8)	0.21 (1.2)	2.51 (15)	4.51 (26)	10.4 (60)	106	
$CaCO_3$ (15.3)	370	5.2 (0.8)	0.09 (0.5)	2.62 (15)	4.62 (26)	7.60 (42)	84	17.9
	193	12 (1.8)	0.08 (0.4)	2.03 (11)	4.71 (26)	8.33 (47)	86	
	12	78 (12)	0.26 (1.5)	2.51 (14)	4.11 (23)	6.86 (38)	89	
	-123	128 (20)	0.26 (1.5)	2.14 (12)	4.12 (23)	9.07 (51)	108	
	-21	100 (15)	0.29 (1.6)	1.30 (7.2)	3.36 (19)	8.94 (50)	93	
	192	14 (2.1)	0.14 (0.8)	2.11 (12)	4.55 (25)	10.6 (59)	99	
	320	12 (1.9)	0.12 (0.7)	2.55 (14)	4.67 (26)	10.9 (61)	104	
Alum (14.5)	399	6.1 (0.9)	0.14 (0.8)	3.03 (17)	4.11 (23)	7.89 (44)	86	17.9
	205	68 (11)	0.23 (1.3)	1.64 (9.0)	3.76 (21)	8.73 (49)	91	
	-17	103 (16)	0.36 (2.0)	1.63 (9.0)	3.38 (19)	8.29 (46)	92	
	-115	127 (20)	0.53 (3.0)	1.28 (7.0)	3.55 (20)	10.7 (60)	110	
	12	118 (18)	0.56 (3.0)	1.49 (8.0)	3.33 (19)	10.4 (58)	106	
	207	12 (1.8)	0.10 (0.6)	1.36 (7.9)	3.99 (22)	10.4 (58)	90	
	334	16 (2.5)	0.16 (0.9)	3.51 (20)	4.23 (24)	7.61 (43)	90	
$FeCl_3$ (1.8)	369	18 (2.7)	0.26 (1.5)	2.83 (1.6)	4.10 (23)	8.17 (46)	89	17.9
	178	138 (21)	0.28 (1.6)	1.35 (8.0)	3.57 (20)	6.74 (38)	89	
	-8	171 (26)	0.49 (2.7)	1.07 (6.0)	3.32 (19)	6.77 (38)	92	
	-94	254 (39)	0.46 (2.6)	0.59 (3.0)	3.33 (19)	8.6 (48)	111	
	-4	243 (38)	0.58 (3.2)	0.51 (3.0)	3.08 (17)	8.8 (49)	110	
	217	43 (6.7)	0.15 (0.8)	1.38 (8.0)	4.48 (25)	8.7 (49)	90	
	362	18 (2.7)	0.08 (0.5)	3.21 (18)	4.22 (24)	8.4 (47)	92	

KCl-RP is loosly-bound P; NaOH-RP is Fe/Al-bound P; and HCl-RP is Ca-bound P. Values in parenthesis are percentages of total P.

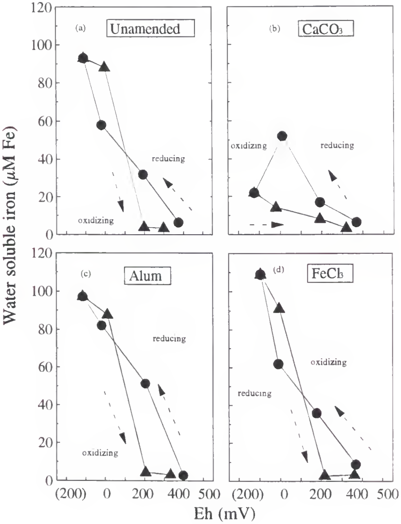

Fig. 5.12. Effect of Eh on dissolved iron concentration in porewater of unamended Lake Apopka marsh soil and chemically amended soils. (a) unamended soil, (b) $CaCO_3$ amended soil, (c) alum amended soil, and (d) $FeCl_3$ amended soil.

5.2). Exchangeable Ca (KCl-extractable) for all soils decreased to a minimum around 0 and -100 mV. The $CaCO_3$ amended soil had lower exchangeable Fe (KCl-extractable) as compared with other soils (Table 5.4). Oxalate-, KCl-, and HCl-extractable Fe for all soils responded to changes in Eh, while CDB-extractable Fe decreased significantly at about 200 mV, followed by minimal changes when Eh levels of soils were subsequently decreased (Table 5.5).

Solubility of P Compounds in Soil Suspension

Calculated solubility diagrams (Fig. 5.13) show that P solubilities in unamended soil and $FeCl_3$ and alum amended soils were undersaturated with respect to solid phases of Ca-P compounds. This suggests that P solubility in these slightly acidic systems was controlled by solid phases other than Ca-P compounds. In $CaCO_3$ amended soils, however, P solubility may be regulated by the solid phases of Ca-P compounds. As the Eh decreased, P equilibrium approached supersaturation levels with respect to beta-tricalcium and octa-calcium phosphate.

Based on the solubility diagram, it is likely that DRP in unamended soil and $FeCl_3$ and alum amended soils was controlled by the solid phases of variscite-gibbsite and strengite-soil Fe (Fig. 5.14). Dissolved reactive P under the highly reduced conditions ($Eh < 0$) appeared to be in equilibrium with either vivianite-soil Fe or variscite-kaolinite.

Ion activity products, calculated using the soil-solution model SOILCHEM, indicated that the unamended soil was undersaturated with respect to Ca phosphates at most Eh levels except under highly reduced conditions (-110 mV) (Table 5.6) and was supersaturated with respect to Al and Fe phosphates under both aerobic and anaerobic

Table 5.4. Extractable (1M KCl) Ca, Mg, Al, and Fe in unamended (Control) and chemically amended Lake Apopka marsh soils at different Eh levels.

Amended Soils	Eh	pH	1 M KCl Extractable (mmol kg^{-1})			
(rate, g kg^{-1})	(mV)		Ca	Mg	Al	Fe
Control	377	5.63	360	102	0.17	0.05
	194	5.65	317	91	0.13	1.00
	-18	5.55	303	87	0.22	2.43
	-110	5.67	294	86	0.19	2.90
	-14	5.68	251	80	0.00	2.60
	199	5.64	279	86	0.00	0.10
	300	5.43	290	92	0.09	0.03
$CaCO_3$ (15.3)	370	6.67	386	95	0.17	0.04
	193	6.65	361	92	0.13	0.07
	12	6.62	437	110	0.31	0.40
	-124	6.12	346	88	0.24	0.40
	-20	5.90	265	71	0.00	0.63
	195	5.56	322	86	0.00	0.03
	320	5.43	288	78	0.00	0.01
Alum (14.5)	399	5.45	368	100	0.18	0.06
	205	5.65	330	88	0.25	2.00
	-15	5.61	323	88	0.23	4.70
	-114	5.70	291	86	0.00	5.10
	12	5.60	283	84	0.00	4.20
	204	5.45	302	87	0.00	0.13
	334	5.36	330	78	0.00	0.03
$FeCl_3$ (1.8)	369	5.51	377	95	0.18	0.05
	178	6.17	303	86	0.25	2.10
	-8	5.55	303	89	0.24	3.00
	-95	5.59	280	86	0.00	3.60
	-3	5.30	245	76	0.00	1.80
	216	5.27	283	88	0.00	0.24
	362	5.16	229	68	0.00	0.01

Table 5.5. Extractable Ca, Mg, Al, and Fe in unamended (Control) and chemically amended Lake Apopka marsh soils at different Eh levels.

Amended Soils	Eh	pH	1 M HCl Extractable				Oxalate Ext.		CDB Ext.		$CuCl_2$ Ext.
			Ca	Mg	Al	Fe	Al	Fe	Al	Fe	Al
(Rate, g kg^{-1})	(mV)		---------------------------------mmol kg^{-1} ---------------------------------								
Control	77	5.63	1133	194	48	71	50	105	44	91	21
	94	5.65	976	164	44	97	42	87	37	84	20
	-18	5.55	980	161	42	100	41	81	24	75	18
	-110	5.67	949	155	41	100	41	75	28	70	17
$CaCO_3$	370	6.67	1298	192	48	71	49	103	44	88	20
(15.3)	193	6.65	1194	179	45	73	44	92	31	64	19
	12	6.62	1208	179	43	102	41	88	37	85	18
	-124	6.12	1155	168	43	101	39	81	27	75	19
Alum	399	5.45	1087	171	94	72	99	103	88	89	47
(14.5)	205	5.65	965	156	78	96	83	87	76	83	36
	-15	5.61	942	151	80	98	85	85	85	94	38
	-8	5.55	939	151	76	98	81	88	74	74	72
$FeCl_3$	369	5.51	1112	188	47	79	48	113	44	95	21
(1.8)	178	6.17	997	167	42	108	43	101	28	81	38
	-8	5.55	931	156	39	108	40	92	31	86	17
	-95	5.59	954	158	41	107	41	88	33	85	55

Oxalate is ammonium oxalate; CDB is citrate-dithionite-bicarbonate.

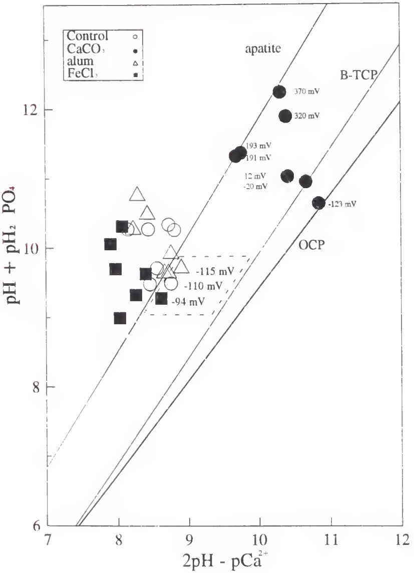

Fig. 5.13. Calculated solubility diagram of Ca phosphate compounds and P solubility changes in porewater of unamended Lake Apopka marsh soil and chemically amended soils, as influenced by Eh and pH.
β-TCP: beta tri-calcium phosphate, OCP: octa-calcium phosphate

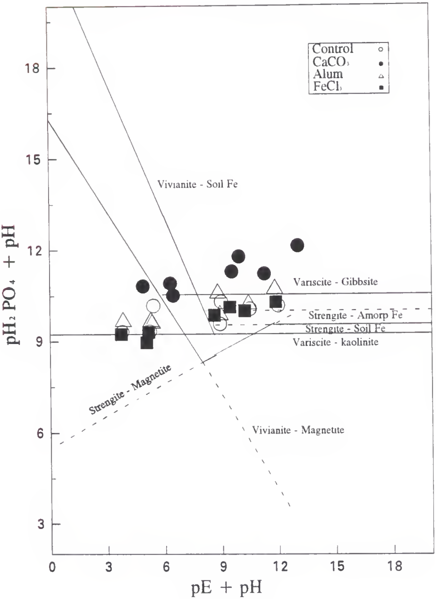

Fig. 5.14. Calculated diagram of Al/Fe compounds and P solubility change in porewater of soils, as influenced by pE and pH. Each line stands for an equilibrium between two compounds. It also shows some specific redox potential at which strengite and variscite can transform into vivianite or vice versa at specific pH, Eh, and P concentration.

Table 5.6. Calculated pK values of selected Ca phosphate minerals in the porewater of unamended (Control) and chemically amended Lake Apopka marsh soils as influenced by various different redox potential.

Sample (Rate, g kg^{-1})	Eh (mV)	pH	Brushite $CaHPO_4$ $2H_2O$ pK= -0.63	Monetite $CaHPO_4$ pK= -0.3	HPA $Ca_5(PO_4)_2OH$ pK= -14.16	B-TCP B-$Ca_3(PO_4)_2$ pK= -10.18	OCP $Ca_4H(PO_4)_3$ $2.5H_2O$ pK= -11.76
Control	377	5.63	2.12	2.12	-9.94	-3.91	-1.79
	194	5.65	1.16	1.16	-13.6	-6.24	-5.09
	-18	5.55	1.01	1.01	-13.9	-6.42	-5.40
	-110	5.67	0.73	0.73	-15.3	-7.29	-6.56
	-14	5.68	1.45	1.45	-13.3	-5.90	-4.44
	199	5.64	1.61	1.61	-12.6	-5.51	-3.91
	300	5.43	1.82	1.82	-11.4	-4.79	-2.97
$CaCO_3$	370	6.67	1.92	1.92	-14.9	-6.48	-4.56
(15.3)	193	6.65	1.50	1.50	-16.3	-7.39	-5.88
	12	6.62	0.61	0.61	-18.9	-9.18	-8.56
	-124	6.12	0.28	0.28	-20.5	-10.1	-9.82
	-20	5.90	-0.21	-0.21	-22.3	-11.3	-11.5
	195	5.56	1.63	1.63	-14.5	-6.40	-4.77
	320	5.43	1.62	1.62	-14.7	-6.53	-4.91
Alum	399	5.45	2.47	2.47	-9.18	-3.35	-0.89
(14.5)	205	5.65	1.16	1.16	-14.1	-6.45	-5.29
	-15	5.61	1.03	1.03	-14.3	-6.62	-5.59
	-114	5.70	0.79	0.79	-15.4	-7.31	-6.51
	12	5.60	0.91	0.91	-14.7	-6.89	-5.97
	204	5.45	2.06	2.06	-10.7	-4.30	-2.24
	334	5.36	2.05	2.05	-10.3	-4.13	-2.09
$FeCl_3$	369	5.51	2.25	2.25	-9.39	-3.56	-1.32
(1.8)	178	5.68	1.00	1.00	-14.2	-6.62	-5.62
	-8	5.55	1.08	1.08	-13.2	-6.09	-5.01
	-95	5.59	0.66	0.66	-15.2	-7.30	-6.63
	-3	5.30	0.97	0.97	-13.2	-6.09	-5.12
	216	5.27	1.81	1.81	-10.5	-4.35	-2.55
	362	5.16	2.17	2.17	-9.29	-3.56	-1.39

HPA: Hydroxyapatite, β-TCP: Beta tri-calcium phosphate, OCP: Octa-calcium phosphate.
All pKs are cited from "Chemical Equilibria in Soil" (Lindsay, 1979)

conditions (Table 5.7). Strengite ($FePO_4$) and soil $FePO_4$ apparently were shown as dominating Fe minerals under aerobic conditions (≥200 mV), whereas vivianite ($Fe_3(PO_4)_2$) may be formed under reduced conditions (≤200 mV). Results suggest an Eh of about 200 mV was critical in Fe reduction in this soil.

Discussion

Initial aerobic conditions prevailed in the system even after a few hours of N_2 addition. This may be due to the presence of oxygen trapped in the soil and dissolved O_2 in the floodwater. The initial decrease in pH, following N_2 bubbling was probably due to CO_2 accumulation and decomposition of organic matter. Later, however, the pH increased gradually under reduced conditions. This increased pH may be due to chemical reduction, which consumes a proton as follows (Ponnamperuma, 1972):

$$3Fe(OH)_3 + H^+ + e^- = Fe_3(OH)_2 + H_2O$$

All treatments (unamended, alum, and $FeCl_3$ amended soils), except $CaCO_3$, showed similar Eh changes. Soils amended with $CaCO_3$ showed rapid decreases to 200 mV (3 to 4 weeks) compared with the other soils (Fig. 5.4). Soils amended with $FeCl_3$ showed a relatively slow Eh change due to the poising effect of added Fe. Rapid decrease in Eh observed in $CaCO_3$ amended soils may be explained with increased pH to 7, which is the optimal condition for the maximum microbial activity for reduction of inorganic electron acceptors (Reddy and Patrick, 1984; Reddy and D'Angelo, 1994).

Dissolved Fe concentration in unamended soil increased from 6.6 μM at 377 mV to about 93 μM at -110 mV, while NO_3^- concentrations (1550 μM and 1300 μM) were

Table 5.7. Calculated pK values of selected Al/Fe phosphate minerals in porewater of unamended (Control) and chemically amended Lake Apopka marsh soils as influenced by various different redox potential.

Sample (g kg^{-1})	Eh (mV)	pH	Berinite $AlPO_4$ pK= -0.5	Variscite $AlPO_4$-$2H_2O$ pK= 2.5	Wavellite $Al_3(PO_4)_2$-OH_3 $5H_2O$ pK= 35	Strengite $FePO_4$-$2H_2O$ pK= 6.85	Vivianite Fe_3(PO4)$_2$-8H2O pK= -3.11	$FePO_4$ (soil) pK= 5.37
Control	377	5.63	-0.25	-0.25	31.1	4.09	-2.60	4.09
	194	5.65	-1.02	-1.02	29.4	2.44	-4.93	2.44
	-18	5.55	-0.63	-0.63	30.8	-2.84	-10.2	-2.84
	-110	5.67	-0.86	-0.86	30.1	-3.20	-10.8	-3.20
	-14	5.68	-0.08	-0.08	31.6	-1.85	-8.69	-1.85
	199	5.64	0.26	0.26	32.5	3.30	-3.28	3.30
	300	5.43	0.06	0.06	32.1	6.54	3.51	6.54
$CaCO_3$	370	6.67	1.86	1.86	35.4	5.43	-2.48	5.43
(15.3)	193	6.65	1.31	1.31	34.1	5.19	-2.97	5.19
	12	6.62	-4.34	-4.34	18.1	-4.33	-13.3	-4.33
	-124	6.12	-10.0	-10.0	0.98	-4.53	-13.9	-4.53
	-20	5.90	-3.42	-3.42	21.2	-5.26	-14.9	-5.26
	195	5.56	1.00	1.00	33.7	4.08	-3.22	4.08
	320	5.43	0.94	0.94	33.9	4.91	-2.46	4.91
Alum	399	5.45	0.91	0.91	34.0	5.07	-0.55	5.07
(14.5)	205	5.65	-0.47	-0.47	30.7	4.78	-2.29	4.78
	-15	5.61	-0.51	-0.51	30.8	-2.79	-9.94	-2.79
	-114	5.70	-0.77	-0.77	30.0	-3.14	-10.6	-3.14
	12	5.60	-0.98	-0.98	29.4	-2.83	-10.1	-2.83
	204	5.45	0.59	0.59	33.2	4.65	-1.12	4.65
	334	5.36	0.48	0.48	33.2	4.61	-1.24	4.61
$FeCl_3$	369	5.51	-0.16	-0.16	31.2	4.08	-2.13	4.08
(1.8)	178	5.68	0.00	0.00	31.9	3.93	-4.45	3.93
	-8	5.55	-0.37	-0.37	31.6	-2.64	-9.78	-2.64
	-95	5.59	-1.04	-1.04	29.6	-3.17	-10.7	-3.17
	-3	5.30	-0.68	-0.68	31.0	-2.52	-9.46	-2.52
	216	5.27	0.40	0.40	33.3	3.94	-1.99	3.94
	362	5.16	0.50	0.50	33.5	4.65	-0.80	4.65

All pKs are referred from “Chemical Equilibria in Soil “ (Lindsay, 1979).

detected only at maximum oxidation conditions during the reduction and reoxidation cycle. Dissolved Fe and Mn concentration also increased significantly at about 200 mV and further increased as the Eh was lowered during the reduction cycle (Table 5.2). During the reoxidation cycle, dissolved Fe concentration was maximum at around -100 mV and remained high to about -10 mV and then decreased drastically at about 200 mV. Iron concentration at about 200 mV during the reduction cycle was higher than that at same level of Eh during the reoxidation cycle. This suggests that high soluble Fe concentration at 200 mV during reduction cycle was attributed to organic matter mineralization. Water soluble Fe concentrations for $CaCO_3$ amended soil were shown to be suppressed as compared to other soils under the reduction conditions (Fig. 5.12 b), indicating that siderite ($FeCO_3$) was probably precipitated under anaerobic conditions (Ponnamperuma, 1972). Increased carbonate ions (CO_3^{2-}) concentration due to disassociation of $CaCO_3$ amendment provided more chances of siderite formation in the anaerobic conditions.

The presence of NO_3^- also retards the reduction of other components just as oxygen retards nitrate reduction. The oxidized manganese and NO_3^- were reported to buffer Eh in the range of 100 mV to 300 mV at pH 7 (Ponnamperuma, 1972; Patrick, 1981; Reddy, 1992). Manganese follows nitrate in the reduction sequence, even though it is used as an electron acceptor in respiration by only a limited number of bacteria. Although the results did not show critical redox potential for each electron acceptor, nitrate reduction was terminated and Mn/Fe begant to be reduced even at Eh higher than about 200 mV in the soils. Similar result was reported in earlier work by Patrick (1964) that a decrease in

Eh around 200 mV resulted in a very large release of ferrous iron. These results indicate that after O_2 was depleted from the suspension, high NO_3^- concentrations buffered Eh for a period of about seven weeks. The long time needed to obtain highly reduced conditions was attributed to the presence of Mn^{4+} and Fe^{3+} compounds.

The retardation of reduction was also due to the acidic conditions in the soils. Slow Eh reduction in unamended and alum and $FeCl_3$ amended soils was attributed to low pH as compared to $CaCO_3$ amended soils. When Eh values were adjusted to pH 7, trends in all soils were found to be similar. Conclusively, the retardation of reduction may be explained by: 1) relatively high concentration of dissolved Fe and the extremely high NO_3 concentration (Patrick, 1977), and 2) insufficient decomposable organic matter in soils (Ponnamperuma, 1972; Sah and Mikkelsen, 1989).

Dissolved reactive P (DRP) concentrations in unamended soil and $FeCl_3$ amended soils responded sensitively to different Eh values, indicating that reduction of Fe is responsible for releasing P in the soils. The soil amended with $CaCO_3$ was least affected in DRP concentration by Eh changes and followed by alum amended soil, indicating that newly added Ca and Al were efficient in immobilizing DRP under anaerobic conditions. The results clearly indicated that water soluble and exchangeable P in Lake Apopka marsh soils were mainly controlled by Fe-bound P. The results from the P fractionation study further showed that the NaOH-RP of the soils decreased significantly with Eh, revealing that the Fe-bound P fraction could be much higher than Al-bound P under aerobic conditions. About 85% of the NaOH-extractable P under very oxidized conditions was lost under highly reduced conditions. This result indicated that the NaOH-extractable P was insignificant in controlling P concentration under highly reduced conditions. The released P by reducing Fe was not taken up by either Al or Ca presents in the soils (Table 5.3). The NaOH-RP does not distinguish between Fe-bound and Al-bound P (Hieltjes and Lijklema, 1980; van Eck, 1982; Psenner et al., 1988).

Soils amended with $CaCO_3$ and alum were effective in reducing DRP concentrations by 83 and 80%, respectively, under oxidized conditions but only 48% under reduced conditions for both treatments. A decrease in NaOH-RP under reduced conditions was responsible for the increased DRP concentrations in both $CaCO_3$ and alum amended soils. The soils amended with $CaCO_3$ and alum, however, had less reduction in NaOH-RP under highly reduced conditions as compared with unamended and $FeCl_3$ amended soils. Added Al and Ca probably contributed to formation of Ca- and Al-bound P in both lime and alum amended soils, resulting in less Fe-bound P under reduced conditions.

A considerably increased DRP concentration (135 μM P) observed at 194 mV during the reduction cycle was higher than the DRP concentration (33.4 μM P) at the same Eh level (199 mV) during reoxidation cycle (Table 5.3). The same trends in the DRP changes were also observed in alum and $FeCl_3$ amended soils. The increased P at 194 mV may have included the result of mineralization of microbial P (Sinke and Cappenberg, 1988), hydrolysis of polyphosphates in bacteria cells (Gachter et al., 1988), and amorphous P compounds. Organic matter under aerobic conditions increases DRP concentration in flooded soil (Meek et al., 1979). Organic matter under reduced conditions, however, intensifies soil reduction processes, causing the transformations of soil Fe and P minerals, and provides more sites for P sorption (Sah et al., 1989).

Transformed and reduced amorphous Fe is reoxidized and reprecipitated with released P under aerobic conditions. A reduced soil has many more sorption sites as a result of the reduction of the insoluble ferric oxyhydroxide compounds to more soluble ferrous oxyhydroxide compounds. Surface active ferrous compounds are one of the major microbial processes affecting P (Patrick and Khalid, 1974). Even though reduction increases the sorption sites, the large number of sites have a lower bonding energy for P than do the smaller number of sites available in the aerobic soil. These results may support a mechanism in which the oxygenated surface layer between the floodwater and soil can act as a sink for phosphate and plant nutrients (Hutchinson, 1957; Ponnamperuma, 1972) in Lake Apopka marsh soils. The redox potential for the oxygenated surface layer of Lake Apopka marsh soil was shown to be about 200 mV (see Chapter 3).

The KCl-RP responded proportionately with the Eh changes, while the NaOH-RP decreased with an Eh increase, suggesting that increased DRP and exchangeable P (KCl-RP) were attributed to the reducible Fe-bound P compounds. Thus, the Fe-bound P may play more dominant roles in immobilizing P in Lake Apopka marsh soils than Al-bound P under aerobic conditions, whereas under reduced conditions, the Fe-bound P becomes a P source rather than a sink (Olila, 1992). The previous incubation test, described in Chapter 3, indicated that a much higher amount of alum than $FeCl_3$ was required to immobilize P in the floodwater of Lake Apopka marsh soil. It was hypothesized that Al in Lake Apopka marsh soil was largely involved in metallo-organic complexes, which are relatively thermodynamically stable (Levesque and Schnitzer,

1967) and hence was not directly involved in P reactions. Hsu (1976) also reported that Fe has more affinity than Al for P in pure water solution.

Calcium- and magnesium-bound P (HCl-RP) in all soils also responded to the Eh changes, possibly because the P left over in soils due to incomplete extraction by 0.1 M NaOH may be trapped by 0.5 M HCl extraction (Fig. 5.8 c). Moore (1992) suggested that Al/Fe-bound P transformed to Ca-bound P due to the increased pH by NaOH solution was probably extracted with the HCl solution.

The solubility product diagram for porewaters of the unamended soil and alum and $FeCl_3$ amended soils showed an undersaturation with respect to Ca-bound P compounds when the Eh of suspensions were higher than 0 mV (Fig. 5.13). The acidic conditions of the soil suspensions ($pH \leq 5.6$) and low P concentration may have moved the points out of equilibrium with respect to Ca-bound P compounds. The solubility diagram also showed that the suspensions were at equilibrium or supersaturated with respect to apatite when they were reduced to less than an Eh of 0 mV. This diagram explains the Fe/Al-bound P could control P concentration under only aerobic conditions for the unamended soils and $FeCl_3$ amended soils. When the suspensions were reduced, the Ca-bound P compounds controlled the DRP in the porewater. The porewater of $CaCO_3$ amended soils was supersaturated or at equilibrium with respect to apatite and amorphous Ca-bound P compounds. The DRP equilibrium moved to beta-calcium and octa-calcium P as the Eh values decreased. The solubility product diagram for the Al/Fe compounds (Fig. 5.14) showed that the porewaters of all soils except the $CaCO_3$ amended soil fit between the lines of Fe/Al-bound P compounds, mostly strengite-amorphous Fe systems and variscite-gibbsite systems. This solubility product diagram also indicated that vivianite could be formed in all soil suspensions when those were under highly reduced conditions.

Although apatite, known as the most thermodynamically stable P compound, has been reported to control P concentrations in natural water systems (Anderson, 1975), it was not, however, expected to precipitate in Lake Apopka marsh soil. This soil has very high amounts of Mg and organic acids, which are known to inhibit the formation of apatite (Martens and Harriss, 1970; Inskeep and Silvertooth, 1988). Analysis of X-ray diffraction data showed that no crystalline P minerals were formed in Lake Apopka marsh soil and its chemically amended soils (see Chapter 3).

Conclusions

Redox potential (Eh) had significant effects on the dissolved reactive phosphorus (DRP) of Lake Apopka marsh soil and the chemically amended soils. Dissolved Fe and Mn concentrations in porewater also responded to changes in Eh. Concentrations of DRP and dissolved Fe in porewater of unamended soils at Eh about -100 mV were about 8 and 10 times higher than those in aerobic conditions, respectively. The increased DRP concentration was due to the released P from reducible Fe compounds. The released P from the reducible Fe and Mn compounds may be mainly responsible for the high floodwater DRP concentration of Lake Apopka marsh soil during the column incubation test (see Chapter 3). Conversely, the DRP and dissolved Fe concentrations decreased at about 200 mV and returned to the original concentrations at around 400 mV during repeated aerobic cycles of the system. Iron oxidized around 200 mV in this acidic soil, suggesting that applying $FeCl_3$ amendments on the oxygenated surface layer that forms between the water and soil column could block rising P from the soil column through adsorption and/or precipitation of P with the oxidized iron. The P fractionation study also showed that the NaOH-RP fraction began to change at 200 mV and decreased drastically at 0 and -100 mV.

Under aerobic conditions, all chemically amended soil decreased porewater P solubility as compared to unamended soils, whereas under anaerobic conditions, the soils amended with $CaCO_3$ and alum minimized the effects of changes in Eh. The increased HCl-RP in the soils amended with alum/$FeCl_3$ was probably due to freed Ca ions extracted by increased acidity through alum and $FeCl_3$ treatments. This result was supported by the increased water soluble Ca concentration in the alum and $FeCl_3$ amended soils (Table 5.4). The freed Ca may have reacted with the water soluble P.

Results from the P fraction study of the unamended soil showed increased (or unchanged) HCl-RP and decreased NaOH-RP compared to results from the previous fractionation study conducted for the soil characterization. The results indicated that NaOH-bound P was probably more soluble than HCl-bound P. It is assumed that P in NaOH-RP is in very amorphous forms and/or complexed with organic acids and Al/Fe (organo-metal-P). Significantly Increased $CuCl_2$-extractable Al in alum amended soil suggests that organo-metal-P complex was formed by added Al. In all soil suspensions, the NaOH-RP fraction changed dramatically as Eh changed and the HCl-RP fraction changed only slightly (Table 5.3).

Soils amended with $CaCO_3$ showed the least effect of Eh changes on DRP, Fe, and NaOH-RP, followed by alum amended soils. Alum and $CaCO_3$ amended soils decreased the DRP concentration in the porewater significantly under both aerobic and anaerobic conditions. Results indicated that most of the released P from the reducible P compounds could not be held by preexisting Al and Ca in Lake Apopka marsh soil. It is believed that newly added Ca and Al could inactivate the released P from reducible metal P forms. Preexisting Al and Ca were probably combined with organic acids, such as humic and fulvic acids, which are believed to have a relatively high affinity for metals.

This study revealed that Fe-bound P is a major fraction of NaOH-RP and Fe is most important controlling factor in P solubility in the Lake Apopka marsh soils. Thus, $FeCl_3$ treatment should be considered carefully because of its sensitivity to redox potential. Alum treatment may be recomendable for immobilizing P in Lake Apopka marsh soil because it is not affected by redox potential changes. Lime materials such as $CaCO_3$ and $Ca(OH)_2$ are more recommendable than alum and $FeCl_3$ not only because of their effectiveness in immobilizing P under heavily reduced conditions, but also low solubilities of Ca-P compounds in this soil. Formation of Al/Fe-bound P compounds are also expected in the increased soil pH (around 6 to 7) by liming the soil. Ferric chloride, however, may be applied to water column or oxygenated layer in the top soil.

CHAPTER 6
INORGANIC CHEMICAL REACTIONS WITH PHOSPHORUS: SYNTHESIS

Constructed wetlands are now regarded as low-cost alternatives to treat nutrient enriched water. Frequent hydrologic fluctuations resulted in creating an aerobic and anaerobic interfaces in the wetland. These interfaces were shown to be one of the major factor influencing biogeochemical cycling of nutrients and metals in the wetland.

There is also growing interest in the conversion of agricultural lands located near aquatic system to wetlands to create a buffer zone. Flooding these lands increases the solubility of residual P, thus resulting in a rapid initial flush of P from soil to the water column. It was hypothesized that application of inorganic amendments containing P binding metals(Ca, Al, and Fe) to wetland soil can reduce P mobility significantly within a relatively short period as compared to stabilization using plants. Each chemical amendment ($CaCO_3$, $Ca(OH)_2$, alum, and $FeCl_3$) has its own advantage in combining with P under specific conditions. To determine the effectiveness of these amendments several laboratory studies were conducted on the reactivity and mobility of P in Lake Apopka marsh soils. The following questions were addressed in these studies.

1) **What is the short-term response of chemical amendments in binding the labile pool of P ? How does the application of amendments influence soil pH and metal concentrations?**

All amended soils were potentially effective in decreasing dissolved reactive P(DRP) in the soil porewater. Unamended Lake Apopka marsh soil released about 1.6 mmol P kg^{-1} to the porewater. The ranges of effective rates required for each amendment to minimize P release from the soil were 15 to 23 g kg^{-1} and 17 to 30 g kg^{-1} for $CaCO_3$ and $Ca(OH)_2$, respectively. Up to 62% and 89% reduction of the water soluble P was immobilized by the application of $CaCO_3$ and $Ca(OH)_2$ amendments, respectively. Reduction of water soluble P was proportional to the added amounts of $FeCl_3$ and alum. To remove more than 80% of water soluble P, rates higher than 12 and 7 g kg^{-1} of alum and $FeCl_3$ amendments, respectively, were needed.

Lime materials such as $CaCO_3$ and $Ca(OH)_2$ at 15 and 17 g kg^{-1}, respectively, increased water-soluble Ca. This suggests that water-soluble Ca concentrations were closely related to the DRP concentration. Soils amended with $Ca(OH)_2$ increased water soluble Ca more than did $CaCO_3$ amendments at their highest rates, whereas the water-soluble Mg concentration decreased dramatically at the highest rate of $Ca(OH)_2$ amendment. Alum and $FeCl_3$ amendments increased water-soluble Ca and Mg concentrations more than did $CaCO_3$ and $Ca(OH)_2$ amendments. This indicates that increased acidic conditions from added alum and $FeCl_3$ probably solublized more Ca and Mg. Soils amended with $CaCO_3$ and $Ca(OH)_2$ increased pH by 0.8 and 2.2 units, respectively, with their highest rates, whereas alum and $FeCl_3$ amendments decreased pH by 0.45 and 0.55 units, respectively. The control soil pH was 5.5.

2) **(a) To what extent can the application of chemical amendment decrease the flux of P from soil to overlying floodwater, and (b) Can the application of the amendments at the soil surface create a sink for soil P?**

In the unamended soil (Control) column floodwater DRP (dissolved reactive P) concentrations increased from 150 μM P up to 1000 μM P during 12 weeks. The DRP concentration in the floodwater decreased at amendment application rates of 15 and 11 g kg^{-1} for the $CaCO_3$ and $Ca(OH)_2$, respectively. The highest rate of $Ca(OH)_2$ amendment further increased P immobilization. The floodwater DRP concentrations of the alum amended soil cores decreased at an application rate of 14.5 g kg^{-1}, while the low rate of $FeCl_3$ (1.8 g kg^{-1}) was effective in immobilizing P. Oxidized forms of oxyhydroxides Fe from the added $FeCl_3$ were probably precipitated on the oxygenated interface between the floodwater and soil column. Also, more water-soluble reduced metals (Fe^{2+} and Mn^{2+}) resulting from soil redox processes probably diffused into the oxygenated interface and reoxidized. The reoxidized metals such as Fe in this aerobic interface, probably resulted in precipitation of DRP in the floodwater. Based on P flux calculations during a 12-week flooding period, the effectiveness of the chemical amendments was in order of: $FeCl_3$ (1.8 g kg^{-1}) > alum (14 g kg^{-1}) > $Ca(OH)_2$ (11 g kg^{-1}) > $CaCO_3$ (15 g kg^{-1}) > dolomite (170 g kg^{-1}). Alum treatment, however, decreased the DRP concentration effectively at the rates higher than 14.5 g kg^{-1}.

Soil P fractionation studies showed that there was more Ca-bound P (HCl-extractable) than Al/Fe-bound P (NaOH-extractable) in Lake Apopka marsh soil. The P solubility diagram also indicated that Ca-bound P compounds controlled P solubility in the floodwater. More soluble Ca P compounds such as β-tricalcium and octacalcium phosphate rather than crystalline Ca P compound (apatite) were expected to form in the Lake Apopka marsh soil due to their high organic acids and high Mg activity . The solubility diagram for Al and Fe P compounds showed that amorphous Al and Fe P compounds rather than crystalline Al/Fe P compounds such as variscite and strengite controlled P in Lake Apopka marsh soil. No crystalline compounds were detected by X-ray diffraction analysis in native or the chemically amended soils.

3) **What is the P binding capacity of chemically amended soils? Soils were chemically amended at the following rate and incubated for 12 weeks under flooded conditions: $CaCO_3$ (15 g kg^{-1}), $Ca(OH)_2$ (11 g kg^{-1}), dolomite (25 g kg^{-1}), alum (14.5 g kg^{-1}), and $FeCl_3$ (1.8 g kg^{-1}).**

The S_{max} (maximum sorption capacity) of the soils amended with lime materials was as follows: dolomite < $CaCO_3$ < $Ca(OH)_2$. Alum treatment resulted in the highest S_{max}, while the $FeCl_3$ treatment gave the lowest S_{max}. Only a portion of previously sorbed P could be readily desorbed. For example, the desorption of P from soil amended with $CaCO_3$ and $Ca(OH)_2$ were 48% and 26% of the adsorbed P, while alum and $FeCl_3$ amendments gave 52% and 60%, respectively, indicating that newly formed Al/Fe-bound P was more soluble than newly formed Ca-bound P. The S_{max} of the lime-amended soils was positively correlated with water-soluble Ca, HCl-extractable Ca/Mg, $CuCl_2$-extractable Al, and HCl-extractable Al/Fe. The S_{max} of the alum and $FeCl_3$ amendments was strongly associated with CDB-extractable Al, oxalate-extractable Al, HCl-extractable Al/Fe, $CuCl_2$-extractable Al, and water-soluble Ca. Results suggest that P was sorbed by the solid phases of both Fe/Al and Ca/Mg compounds.

4) **How do the changes in redox potential (Eh) of chemically amended soils affect the solubility of P and associated metals**?

The concentrations of DRP and Fe increased by 8 and 10 times, respectively when the soil Eh reached -100 mV. Conversely, high water soluble P and Fe concentrations maintained under anaerobic conditions decreased rapidly when soils were oxidized and the Eh was increased to 400 mV. The increased DRP concentration in the porewater was due to the reducible Fe-P compounds. The soil amended with $FeCl_3$ showed same trends in DRP and Fe concentrations as unamended soil. The soils amended with $CaCO_3$ and alum showed the least effects of Eh changes on the DRP and metal concentrations.

The soil P fractionation of the air-dried Lake Apopka marsh soil (Control) before flooded showed an evenly distribution of HCl-RP (3.3 mmol kg^{-1}) and NaOH-RP (3.2 mmol kg^{-1}). The soils amended with $CaCO_3$ showed increased levels of HCl-RP, while soils amended with alum and $FeCl_3$ showed increased levels of NaOH-RP compared to unamended soil.

Phosphorus fractionation of the amended soils showed that the NaOH-RP fraction was influenced by Eh, while the HCl-RP fraction was unaffected. The NaOH-RP fraction for the control and $FeCl_3$ amended soil was negligible under the most reduced conditions. Results indicated that the NaOH-bound P may be composed mostly of Fe-bound P. Meanwhile, $CaCO_3$ amendments decreased both DRP and Fe concentrations in the porewater regardless of Eh, while alum treatments decreased floodwater DRP. The results suggested that most of the released P could be held not only by native Al and Ca, but by newly added Ca and Al under reduced conditions.

Synthesis

The results presented in this study show that the capability of Lake Apopka marsh soil to immobilize inorganic P can be improved by amending the soil with various metal salts ($CaCO_3$, $Ca(OH)_2$, alum, and $FeCl_3$). Physico-chemical characteristics of Lake Apopka marsh soil were altered by chemical amendments, resulting in wide differences in P immobilization capability and P distribution.

Lake Apopka marsh soil, characterized by high organic matter content, contains high concentrations of Ca, Mg, Al, and Fe. Concentrations of Ca and Mg were much higher than Al and Fe in the soil and soil pH was slightly acidic (pH = 5.8). Phosphorus fractions of the soil were as follows 5% (1 M KCl-RP), 20% (Fe/Al-bound P), 21% (Ca/Mg-bound P), and 54% (residual organic P). Lake Apopka marsh soil showed little affinity for P according to a high EPC_0 concentration (766 μM P). This was supported by rapid flux of P from soil to overlying water column during 12 weeks of incubation. The high floodwater P and EPC_0 concentrations may be directly related to relatively high water-soluble and exchangeable P. When the soil Eh was reduced to less than 0 mV, porewater P concentration as well as water soluble Fe concentration were drastically increased. This was explained by the release of P and Fe from the reducible Fe-bound P compounds, particularly under the reduced conditions. The results clearly indicated that water soluble P concentration in floodwater of the Lake Apopka marsh was controlled by Fe. Eighty-three percent of Al- and Fe-bound P (NaOH-RP) was released at -110 mV, indicating that most of the NaOH-RP was Fe-bound P. Calcium- and Mg-bound P (HCl-RP) were also shown to be affected by Eh changes even if it was small, suggesting that HCl-RP is explained by Fe in this organic soils. Hsu (1973) reported that the formation of mixed phosphate of Ca and Fe (III) was observed even below pH 5. In mixed systems of Ca and Al or Fe, two types of beneficial effects were suggested: (1) precipitation as mixed phosphate of Ca and Al or Fe and precipitation as Ca phosphate at pH 6.8 and above, (2) precipitation as mixed phosphate of Ca and Al/Fe below pH 6.8 (Hsu, 1975). The calculated solubility diagram and IAP values showed that the floodwater P concentration was supersaturated with respect to apatite, β-tricalcium, and octacalcium phosphates as well as Fe- and Al-bound P compounds. The calculated IAP values for P minerals were only a little higher than K_{sp} values, indicating that the floodwater was saturated with respect to P compounds. There is an agreement that high temperature and 100 times higher IAP values than K_{sp} are usually needed for formation of crystalline P compounds. Organic matter and Mg, each of which were found in relatively high concentrations in this soil, however, have been shown to inhibit apatite formation. Therefore, a more soluble mineral phase, such as octacalcium phosphates, dicalcium phosphate, and other even more soluble complex ($Ca_2[HCO_3]_2PO_4$) and amorphous minerals ($Ca_3[HCO_3]_3PO_4$), may have been forming instead. Such a metastable surface complex ($Ca_2[HCO_3]_2HPO_4$), which is transformed to ($Ca_3[HCO_3]_3HPO_4$, $pK_{sp} = 28.5$) on $CaCO_3$ were suggested to control P concentration in the Jordan river water (Yigal et al., 1993).

Possible sequential reactions after applying of $CaCO_3$ to the soil are as follows:

$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$

$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$

$3OH^- + AlPO_4\ (FePO_4) \rightarrow Al(OH)_3\ (Fe(OH)_3) + PO_4^{3-}$

$PO_4^{3-} + 2H_2O \rightarrow H_2PO4^{2-} + 2OH^-$ ($[H_2PO_4^-] = [HPO_4^{2-}]$ at pH = 7.2)

$H2PO_4^{2-} \rightarrow H^+ + HPO_4^{2-}$ $\log K_{sp} = -7.2$

$Ca^{2+} + HPO_4^{2-} + 2H_2O \rightarrow CaHPO_4{\bullet}2H_2O$ (brushite) ($\log k_{sp} = 6.57$)

$Ca^{2+} + 3HPO_4^{2-} + 2.5H_2O \rightarrow Ca_4H(PO_4)_3{\bullet}2.5H_2O$ (OCP) + $2H^+$

Calcium hydroxide was more effective than calcium carbonate in reducing the water-soluble P concentration. A possible explanation for this is that calcium hydroxide dissociates and forms calcium carbonate (calcite).

$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$

$H_2O + CO_2 \rightarrow CO_3^{2-} + OH^-$

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(S)}$ $\log K_{SP} = 8.3$

These newly formed calcite crystals are small and present a relatively large surface area for P adsorption (Babin, 1992).

$3CO_3^{2-}$ (calcite) + $2PO_4^{3-}$ (aquatic) $\rightleftarrows$ calcite ($2PO_4^{3-}$) + $3CO_3^{2-}$ (aquatic)

By increasing the carbonate concentration through the liming with OH^-, the equilibrium is shifted to the right and P is coprecipitated with calcite crystal. Calcite as a carbonate mineral was detected in the soil amended with $Ca(OH)_2$ by X-ray diffraction analysis. No crystalline calcium P compounds were found, however, in the soils.

As would be expected, redox changes had less effect on DRP concentration in the porewater of soils amended with $CaCO_3$ (see Chapter 5). Water soluble Fe concentration in the porewater of $CaCO_3$ amended soils was suppressed under anaerobic conditions (Fig. 5. 12 b), indicating that siderite ($FeCO_3$) was probably precipitated under anaerobic conditions (Ponnamperuma, 1972; Snoeyink and Jenkins, 1980). Increased carbonate ion (CO_3^{2-}) concentration due to a disassociation of $CaCO_3$ amendment provided more chances of siderite formation in the anaerobic conditions. Increased alkalinity due to the addition of lime materials probably helped dissolve Al/Fe-bound P compounds, resulting in formation of Ca-bound P compounds. The OH^- produced by the cathodic reaction not only may precipitate $Fe(OH)_{2(s)}$ but can also react with bicarbonate ion to produce carbonate ion (Snoeyink and Jenkins, 1980).

$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$

$H_2O \leftrightarrow OH^- + H^+$

$HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-}$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_{3(s)}$ (siderite)

The addition of alum/$FeCl_3$ to solution initially brings in the hydration of Al/Fe with six water molecules to form a hydrated trivalent aluminum ion. This ion then undergoes a series of pH dependent hydrolysis reactions ultimately forming colloidal Al/Fe hydroxide. The Al hydroxide is amphoteric and thus is converted to the soluble aluminate ion in basic solution. The distribution of hydrolyzed Al species is dependent on solution pH: $Al(OH)_3$ is dominant between pH 6 to 8, Al^{3+} is dominant below pH 3 to 4, and aluminate ion is favored above the range of 6 to 8. Iron behaves very much like Al in solution except that Al has greater tendency to form polynuclear species.

$$Al_2(SO_4)_3 \bullet 8\ H_2O \leftrightarrow 2\ Al^{3+} + 3SO_4^{2-} + 8\ H_2O$$

$$Al^{3+} + 6H_2O \leftrightarrow Al(H_2O)_6^{3+}$$

$$Al(H_2O)_6^{3+} + H_2O \leftrightarrow Al(OH)^{2+}(H_2O)_5 + H^+$$

$$Al(OH)^{2+} + H_2O \leftrightarrow Al(OH)_2 + H^+$$

$$Al(OH)_2 + H_2O \leftrightarrow Al(OH)_{3(s)} + H^+$$

$$Al(OH)_{3(s)} + H_2O \leftrightarrow Al(OH)_4^- + H^+$$

$$2Al^{3+} + 2H_2O \leftrightarrow Al_2(OH)_2^{4+} + 2H^+$$

Thus, P removal by Al can occur by precipitation of $AlPO_4$, which is the favored mechanism with high P concentration and low pH, and sorption of phosphates to the surface of aluminum hydroxides floc in natural water. Phosphorus adsorption by an organic acid Al complex is also very important.

The batch incubation study conducted under well mixed conditions showed that porewater DRP concentration of alum/$FeCl_3$ amended soils was proportionally decreased with increased amounts of chemicals. To remove 88% and 82% of the control DRP porewater concentration, rates higher than 14.4 and 7.1 g kg^{-1} of alum and $FeCl_3$, respectively, were required. In the column incubation study, the floodwater DRP concentration was not reduced significantly until the rate increased to 14.5 g kg^{-1} in alum treatment, while the floodwater DRP of soil amended with $FeCl_3$ was decreased dramatically at only 1.8 g kg^{-1}. For alum treatment, 14.5 g kg^{-1} (43 mmol kg^{-1}) was regarded as the effective rate, while for $FeCl_3$ treatment, the effective rate was shown to differ according to the incubation conditions. The reason why the low application rate of $FeCl_3$ was so effective in the column incubation study may be that gel-like ferric oxyhydroxides formed on top of the soil column. Highly water-soluble Fe^{2+} probably diffused up by mass flow and was reoxidized on the oxygenated layer, resulting in Fe-P being precipitated out on the soil surface. In the case of mixing conditions, much of the Al and Fe may be involved in building organo-metal complexes.

A high molar ratio of Al to P (about 33) was required to immobilize DRP in the column incubation studies. Results suggested that the $FeCl_3$ treatments were more adequate for application to the water column or on to the top soil rather than into the soil column. Reactor incubation study conducted under mixing condition (see Chapter 5) supported the result above, that 1.8 g kg^{-1} soil of $FeCl_3$ treatment, which appeared to be the effective rate in the column study (see Chapter 3), gave a relatively high porewater DRP concentration (17.4 μM P) even under aerobic conditions. This concentration was about three times higher than that for $CaCO_3$ treatment (5.17 μM P) and alum treatment (6.05 μM P).

Under anaerobic conditions, the $FeCl_3$ amended soils had drastically increased porewater DRP concentrations and water soluble Fe concentration. Alum treated soil showed fewer effects of redox potential on porewater DRP concentration. Water soluble Al concentrations for alum amended soil, however, was considerably affected by Eh changes (Table 5.2). This may be explained due to a temporary fluctuations in pH as Eh changed.

Alum treatment had 1.28 mmol kg^{-1} of NaOH-RP at the lowest Eh, while at the highest Eh, it was 3.03 to 3.51 mmol kg^{-1}. The difference in the NaOH-RP fraction

(1.75 to 2.23 mmol kg^{-1}) between under aerobic and anaerobic conditions was assumed to be the Fe-bound P fraction. This fraction appeared to be smaller than that of unamended soil (Control) (2.08 to 2.4 mmol kg^{-1}), indicating that a small fraction of Fe-bound P may be transformed to Al-bound P by added Al. If the NaOH-RP fraction shown at the lowest Eh is regarded as Al-bound P, alum treatment could increase it to 1.28 mmol kg^{-1} from 0.43 mmol kg^{-1} of Control.

Aluminum- and Fe-bound P also were a large part of the total inorganic P (about 50 %). Relatively high oxalate- and CDB-extractable Al and Fe concentrations indicated that Al and Fe also were main factors in controlling P concentration in Lake Apopka marsh soil. This soil was shown to have more oxalate-extractable Al and Fe than CDB-extractable Al and Fe, indicating that amorphous Al/Fe P compounds were more favorable in this soil rather than crystalline Al/ Fe P compounds. Calculated ion activity products for Al/Fe P compounds also supported that this soil was supersaturated with respect to amorphous Al and Fe P compounds.

Results showed that Lake Apopka marsh soil has very high potential as a P source to the overlying water column. This study has proved that the capability of Lake

Apopka marsh soil in P immobilization could be increased by amending the soil with metal salts such as alum, $FeCl_3$, $CaCO_3$, and $Ca(OH)_2$. This study, however, also identified some research issues that require future investigation:

(1) Further identification and quantification of Al-bound P and Fe-bound P from the NaOH-RP fraction is needed. The study should include X-ray diffraction analysis and other techniques to verify whether crystalline P minerals are

formed by chemical amendments. Some processes to deal with highly characterized organic soils should be developed for the x-ray diffraction analysis.

(2) The effects of direct changes of pH, CO_3, Mg, and organic acid on P solubility in unamended soil and chemically amended soils need to be studied.

(3) In situ studies on the effective rates of selected chemical amendments for P inactivation in the soil-water column are needed.

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BIOGRAPHICAL SKETCH

Yoeng-Kwan Ann was born in Og-kag, Og-chun, South Korea, on July 3, 1954, the third of five children of Mr. and Mrs. Gik-Soon Ann. He had his early education at Dae-Heung school in Dae-Jun and attended Bo-Moon high school in Dae-Jun for three years and graduated in March, 1973. He entered the Soong-Jun University in Seoul where he finished his B. S. degree in Chemical Engineering, in 1981 after finishing his compulsory duty in army for 3 years. He worked at the Sam-Hwa Capacitor Company for a year. Then he felt like studying more seriously, and went to University of Scranton in Pennsylvania to pursue his master degree in Chemistry. After completing his M. S. degree in 1985, he moved to Baltimore, Maryland to stay with his uncle. He met his wife, Angela at that time. In 1987, he decided to pursue a Ph. D. degree and entered the Environmental Engineering Sciences Department, University of Florida, but he could not support himself to continue his study. Since September 1989 he has pursued a Ph. D. degree in the Environmental Engineering Sciences Department. He is presently a candidate for the degree of Doctor of Philosophy.

Yoeng-Kwan Ann is married to Angela Chummi and they have two daughters, Elisher Eumi and Katherine Bomi.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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